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COCOA BY-PRODUCTS AND THEIR UTILIZATION AS FERTILIZER MATERIALS

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INTRODUCTION

As a result of an interesting economic situation, related to the existing great demand for cacao butter, there are now in the United States three trade residues produced from cacao beans where formerly the husks or shells were the only regular by-product of commercial importance. The two recent arrivals in this field are by-product cocoa press cake and solvent-extracted cocoa, and their advent in important quantities has created renewed interest in the utilization of cacao by-products. All three by-products are available at prices which put them within the reach of the fertilizer industry.

One of these potential fertilizer materials, the by-product cocoa cake, is nothing less than the press cake remaining from the manufacture of cacao butter. The best of it is almost identical in composition with the ordinary powdered cocoa of commerce. Usually, however, a lower grade of cacao bean is used when production of the butter is the chief consideration, and less care may be exercised in the milling operations than when cocoa for human consumption is being produced.

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[1] Cocoa, cacao butter, etc., products derived from the seeds of the cacao tree, are not to be confused with coconut, coconut oil, and copra, obtained from the coconut palm, even though coconut is often written "cocoanut." "Cocoa" as a corruption of "cacao" probably resulted from an early popular confusion in which the coconut was credited with being the source of cocoa and chocolate. Cacao "beans" are small seeds, about 1 inch long and three-fifths of an inch broad, whereas the familiar coconut is nearly as large as a man's head.

The enormous demand for cacao butter has resulted in a great surplus of this by-product cocoa press cake, and thousands of tons of the product have had so low a market value that some of the material has been burned under the factory boilers. Its low price has made the cake available for use as fertilizer material, and at least two manufacturers of mixed fertilizers have given the product a trial as a rough ammoniate filler and conditioner in their mixed goods.

A certain quantity is being subjected to extraction with a fat-solvent for the recovery of the cacao fat remaining in the cake after the hydraulic pressing, and this solvent-extracted cocoa residue also is available for utilization as fertilizer material. The surplus cocoa cake has been used as a source of the alkaloidal base theobromine and it has also been tried as an ingredient of cattle feed.

In view of the quantities of these cocoa by-products available and the dearth of published information relative to their production, chemical composition, and the properties of their nitrogen-bearing constituents, an investigation of their nature and their value as fertilizer material was undertaken.

THE CACAO BEAN AND ITS PRODUCTS

SOURCE

Cacao or cocoa[2] beans, the original source of these by-products and of our chocolate, breakfast cocoa, and cacao butter, are the separated seeds of the fruit of a tropical tree, *Theobroma cacao* L. Van Hall (*19*)[3] states that other species of *Theobroma* yield beans that may be used locally, but only one, *T. pentagona* Bern., is cultivated.

This yields the variety known as "alligator cocoa." It is not of great importance commercially. Knapp (*27*) mentions a third species, *T. sphærocarpa*, but adds that *T. cacao* produces nine-tenths of the world's cacao.

As received at the manufacturing centers in this country and Europe, the beans are ready for roasting, preliminary to cracking and the separation of the valuable kernels or nibs from the shells and germs. The earlier operations of fermenting, cleansing from the fruit pulp, and drying the seeds are invariably performed in the country of origin.

The beans are roasted to develop aroma and improve the flavor of the nibs and to make brittle the tough spermoderm or shell. This facilitates the breaking of the beans and the subsequent separation of the nibs from the shell by-products.

The relative quantity of nib or shell in the raw cacao bean varies with the variety and maturity of the seed and with the preliminary treatment to which it has been subjected. It is believed that the data reported by Knapp and McLellan (*25*) and by Silberberg (*44*) are representative for clean, raw seeds. The percentage of shell obtained by hand separation varied from 7.3 to 15.8, and the percentage of germ from 0.5 to 0.9, the remainder representing the nib. The averages given by Silberberg are—shell 12.1 per cent, germ 0.7 per cent. Knapp and McLellan state that roasting decreases the percentage of shell from 1 to 3 per cent. Winton, Silverman, and Bailey (*60*) separated the shells from 17 samples of carefully roasted beans and found the average content of pure shells in the roasted beans to be 11.54 per cent.

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[2] Cocoa is the correct English term for the powder used in making the popular breakfast drink, but to avoid confusion it is well to adhere to the rule of identifying such products as the shells and the butter by the adjective cacao instead of cocoa. "Cocoa" butter has been confused with coconut oil repeatedly.

[3] The italic numbers in parentheses throughout this bulletin refer to "Literature Cited," p. 41.

The proportion of nibs and by-products obtained from commercial cacao varies with the source of the beans and the manner in which they are prepared. Knapp's figures (*24*) undoubtedly can be accepted as representing the general average for factory practice, at least in England. Starting with 100 pounds of raw beans, as imported, he assumes a loss of 7 pounds in roasting and separating, and gives the average yield as 78.5 pounds of usable nibs (containing 2 per cent of practically inseparable shell material), 10.5 pounds of commercial shells, and 4 pounds of "smalls," which is about one-third fine shell material, and includes the hard, rodlike radicles or germs. From other analyses it is evident that the germs do not amount to more than 12 ounces. American manufacturers have reported yields of 79 to 82 pounds of finished nibs, and losses of 4 to 8 pounds in separating and roasting 100 pounds of raw beans. Evaporation of moisture commonly accounts for from 4 to 6 pounds of the loss, the remainder being due to foreign matter and rejected beans. The refuse material (about 14 pounds) consists of the shells fraction and the "fines," which correspond to the English "smalls" and include the germs, very fine shell and nib particles, and dust. The separated shells fraction may amount to 6 to 12 pounds, depending on the type of equipment and factory practice.

In good practice the nibs are the only portion of the cacao bean used in the manufacture of the primary products. However, absolutely perfect separation of nibs from shells is not attainable in factory work. Several investigators (*22*, *24*, *26*, *44*, *58*) agree that in the nibs or straight chocolate 2 per cent of shell refuse is a fair allowable limit.

PRIMARY PRODUCTS

Chocolate is prepared from the separated nibs by prolonged grinding in special mills. Because of the high content of cacao butter present in the nibs, and a slight heating of the burrstones, the chocolate becomes plastic or fluid in the milling, and this has given rise to the designation "chocolate liquor." "Plain chocolate" is also known to the trade as "chocolate liquor." The fluid chocolate usually is run into molds, in which it solidifies on cooling.

Cocoa or powdered cocoa and "breakfast cocoa,"[4] on the other hand, represent that part of the cacao nibs remaining after expressing a varying proportion of the cacao butter from chocolate liquor, either freshly prepared from the nibs or from cake chocolate. The cacao butter is expressed from the hot liquor in heated hydraulic presses. After removal from the press the cocoa cakes are allowed to cool and are then reduced in disintegrators and finally pulverized to yield cocoa powder. In short, the cocoa press cake, from which cocoa powder or breakfast cocoa is prepared by pulverizing, is merely chocolate deprived of a portion of its fat or cacao butter.

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[4] Breakfast cocoa is cocoa which contains not less than 22 per cent of cacao fat (52).

The expressed butter also may now be considered a primary product of the cacao bean, since the demand for cacao butter has outrun the supply from normal cocoa manufacture. During the last two or three years the market has been extraordinarily favorable to the production of the butter; so favorable that its manufacture, generally, has become economically independent of the commercial value of its complementary product, the press cake. It has paid American manufacturers to grind and press cacao beans for the butter alone, even if dead loss of the press cake had to be assumed.[5] The primary cause of this novel condition is, of course, the enormous demand for cacao butter, but a contributing cause is the low cost of the imported beans concomitant with the protective tariff on the butter.[6]

For many years cacao beans were pressed in order to prepare cocoa powder and the butter was an incidental product. Indeed, in the early days of cocoa manufacture in this country the cacao butter was often a by-product of little value, used to a limited extent as an unguent, as a base for toilet preparations, and in pharmacy. At times profitable disposal of this fat became a real problem to the maker of cocoa. Conditions changed entirely, however, with the development of the great trade in such chocolate confections as milk chocolate, sweet chocolate, and chocolate coatings. In the manufacture of these commodities more cacao butter is required than is present in the chocolate liquor used, so that additional cacao nibs must be deprived of a part of their fat to furnish this extra butter. For a time the quantity of cacao butter produced in the manufacture of cocoa was sufficient to supply the requirements for the special confectionary chocolate trade, and importations of the cheaply produced European butter also helped to maintain the balance when the domestic supply became inadequate.

BY-PRODUCTS

In the past the only important by-product of the industry in the United States normally cheap enough to be of interest to the fertilizer trade has been the husk or shell refuse.[7] There was no such commodity as by-product cocoa cake a few years ago, and of course no solvent-extracted cocoa was produced. Under the new conditions, however, there has not been sufficient increase in the demand for powdered cocoa to take care of the very great increase in the production of the press cake. As a consequence a varying but important proportion of the cake produced has been a drug on the market. Also, since the manufacturer's chief concern has been the production of cacao butter, much of the press cake not intended for use as cocoa powder has been either low grade (too poor in quality to satisfy the legal requirements for powdered cocoa), or pressed "dry" in very powerful presses to a minimum fat content.

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[5] As one manufacturer has pointed out, this does not necessarily mean that the pressing of cacao for its butter is a profitable commercial undertaking by itself, but that under certain market conditions a chocolate manufacturer may be warranted in pressing for butter for his own use, especially if his pressing equipment is not being operated at capacity on regular cocoa.

[6] Under the tariff act of 1922 (*50*), cacao beans are imported duty free, whereas cacao butter is dutiable at 25 per cent ad valorem. Powdered cocoa also bears a duty of 17½ per cent ad valorem, but not less than 2 cents per pound ($40 per ton).

[7] A small amount of the fines may occasionally have been available for use as fertilizer material; but in general this refuse has been burned, it is believed.

In this bulletin the cake produced as a by-product in the manufacture of cacao butter is designated low-grade or by-product cocoa cake, to distinguish it from the cake intended for the preparation of the powder used in making potable cocoa.

The cake has had so little value at times that some manufacturers have used their surplus for fuel in order to get rid of it. Persons familiar with the situation and the material have therefore turned to utilization as fertilizer as offering a more profitable outlet for the surplus cake; and the United States Department of Agriculture from time to time has received samples of the pressed cake with requests that the material be analyzed and its value as fertilizer determined.

The defatted cocoa residue from press cake that has been subjected to solvent-extraction for recovery of its fat, appears to have been of little or no value, except as fertilizer material.

There are, therefore, at the present time three types of cocoa by-products with a market value sufficiently low to make them of interest to the fertilizer trade: (1) The surplus powdered cocoa and low-grade press cake[8]; (2) the fat-free, solvent-extracted cake residue; and (3) the shells.

BY-PRODUCT COCOA PRESS CAKE AND POWDER

One of the first samples of cocoa press cake submitted to the department, with a request from the manufacturer for suggestions as to how the material could be utilized, on examination was found to contain over 23 per cent of cacao fat, and to be similar in composition to "breakfast cocoa."[9] The manufacturer stated that he had a great oversupply of this press cake at the time, with absolutely no demand. In view of the very apparent economic saving to be attained through full and efficient utilization of the constituents of such a product,[10] it was decided (1) to seek information on the quantity of similar material available and the extent to which it was being subjected to solvent-extraction for the commercial recovery of cacao fat, and (2) to ascertain its properties in relation to possible ultimate utilization as fertilizer material.

Authentic information of this sort and statistical data on the production of press-cake residues from the manufacture of cacao butter were not found either in the standard textbooks on the cocoa and chocolate industry, or in the trade journals. Hence it was necessary to seek the desired information directly from the producers. A questionnaire relating to the quantity of the material produced, the quantity available for fertilizer, and the proportion being subjected to solvent-extraction for the recovery of additional fat, was submitted to 24 individuals and firms, of which 17 were known producers of cacao butter in the United States.

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[8] Included with the low-grade cake is a relatively small quantity of fines press cake, which includes the cacao germs.

[9] This material contained somewhat more crude fiber and ash than would be permissible in breakfast cocoa, indicating that less care had been taken in the cleaning and removal of shells.

[10] Cacao butter was quoted at 26 cents per pound at the time, so that the intrinsic value of the fat in 1 ton of the material represented by the sample was over $120.

A majority of the leading establishments (according to classification based on the value of the cocoa, cacao butter and chocolate produced annually) were included among those receiving the questionnaire. The replies and other correspondence received from 12 firms and an association of manufacturers, representative of the cacao industry in America, gave an intimate and fairly comprehensive picture of the situation. This was supplemented in January, 1925, by a visit to several producers and a study of the manufacturing processes at a leading cacao-pressing plant, and at the one establishment practicing the solvent-extraction of cocoa.

Fifty-five establishments were primarily engaged in the manufacture of cacao products at the time of the compiling of the latest published report of the Bureau of the Census (*49*),[11] and it is reasonably certain that most of these plants produce some by-product or surplus press cake and powder. Less than a dozen manufacturers, however, have produced the low-grade cake in important quantities.

PRODUCTION

The following figures on the total production of low-grade cake are estimates based on data obtained in this study. No exact, nation-wide production survey has ever been made for this by-product. The figures obtained directly from producers were tabulated, and the estimates represent the correlation of these data with all other available information.

It is concluded that 15,000 tons is a very conservative estimate of the quantity of low-grade or surplus cocoa cake produced during the calendar year 1923, and the total for that year may have exceeded 21,000 tons. Production apparently increased during 1924, as reliable reports from individuals engaged in the industry indicate that not less than 25,000 tons of the by-product cake was produced during that calendar year. The outlook for 1925 was for at least maintained production.

The greatest annual production of by-product cake actually reported by a single establishment was 3,000 tons for the year 1924.

The segregation of production evident in the cocoa industry should be very favorable to profitable disposal of the low-priced by-product. A large part of the total tonnage produced is localized about such great distributing centers as New York, Philadelphia, and Boston.

Two more or less distinct types of low-grade cocoa cake are being produced. The more common sort is pressed in the ordinary, older style of press used generally in the production of the powdered cocoa of commerce. Such presses are not highly efficient, considered solely from the point of view of the production of the cacao butter, and yield a press cake of rather high fat content, which is desirable when potable cocoa is being made. The by-product or low-grade cocoa cake produced in these presses contains from 15 or 16 to over 20 per cent of fat. The appearance of ordinary cocoa press cake is shown in Figure 1; the brick at the left serves to indicate the relative size of the cakes. Any surplus powdered cocoa originally intended for human consumption, which for one reason or another could not be marketed for that purpose, would also be included in this class.

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[11] Establishments producing cacao products but engaged primarily in the manufacture of chocolate confectionery are not included.

The other type of cocoa press cake is the result of endeavor to increase the yield of cacao butter, without regard to the composition of the residual cake. Very powerful and efficient pressing equipment has been designed and built in recent years especially for the purpose of leaving a minimum amount of cacao butter in the press cake. Cocoa cake produced with such equipment may contain as little as 9 per cent of fat, and is often called dry-pressed cake. Giant presses of the new type have produced cakes running as low as 8 per cent of fat. The average fat content of dry-pressed cocoa cake, however, is probably about 13 per cent, most of it testing between 10 and 15 per cent.

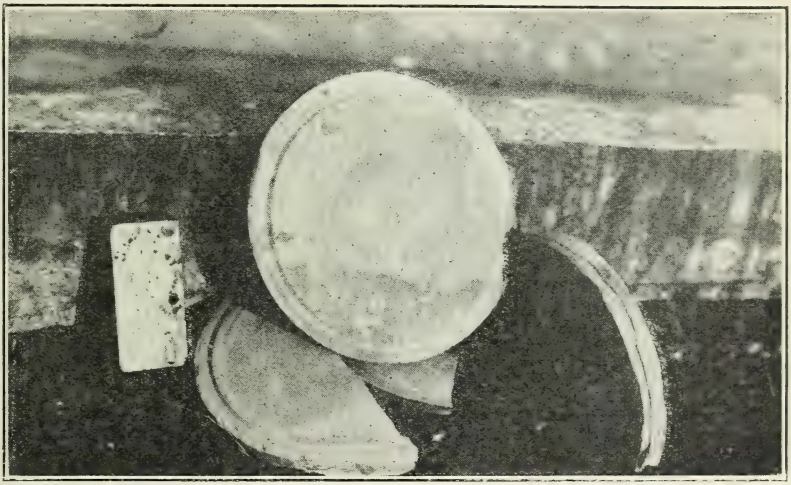

FIG. 1.—Cocoa press cake. The entire disk shows the appearance of the cakes produced in the ordinary type of hydraulic cocoa press

In 1924, although only a few factories were equipped for the production of the dry-pressed cake, the quantity produced amounted to over 4,000 tons.

Another sort of press cake should be mentioned. In at least one factory, where the amount of fines including the germs is said to be 2 to 4 per cent of the weight of raw beans, this material is allowed to accumulate and is then pressed by itself. It is rich in fat, but yields a low grade of butter and cake. (This cake is represented by sample 109, Tables 2 and 3, pp. 14 and 20.) Some of this cake has been sold to manufacturers of complete fertilizers. It is understood that a similar cocoa by-product of another factory is sold for use in the manufacture of cheap chewing tobacco.

YIELDS OF CACAO BUTTER AND PRESS CAKE

The yields of cacao butter and regular nibs press cake from a given weight of cacao beans depend, of course, on the proportion of nibs, the fat-content of the roasted nibs, and the degree to which the pressing is carried. Factors affecting the degree to which the fat is expelled in the press (or conversely the quantity of fat left in the press cake) are: (1) The actual pressure exerted per square inch of cake surface, (2) the temperature at which the pressing is conducted, and (3) the length of time during which the pressure (and temperature) are maintained. The thickness of the layer of liquor pressed and the type of press-mat used also may affect the quantity of butter obtained.

Cocoa presses are commonly operated with a pressure on the hydraulic ram of from 5,000 to 6,000 pounds per square inch. In the giant presses, capable of producing the driest press cake, the ram may be as large as 19 inches in diameter, a diameter greater than that of the pots in which the chocolate liquor is pressed. The actual pressure per square inch of cake surface in such presses may therefore exceed 6,000 pounds.

The temperature at which the liquor is maintained during ordinary cocoa pressing is about 60° C. (140° F.); and probably 40 minutes is the average pressing time. Higher pressing temperatures, though tending to increase the yield of cacao butter, are said to injure the quality of the cocoa. When the highest practicable yield of the butter is the chief consideration, however, that is, when the cake being made is low-grade or by-product cake, its quality is of no moment. Some of the driest low-grade cake encountered is said to have been pressed at a temperature of 90° C. or more for from 55 to 60 minutes. It is claimed that this higher temperature does not injure the quality of the cacao butter.

The liquor from freshly roasted nibs contains only about 1.5 per cent of moisture (*26*), so the loss in weight during pressing, due to evaporation, must be almost negligible. It follows that in ordinary factory practice the sum of the weights of the butter and cake obtained very nearly equals the weight of chocolate liquor pressed.

The following data on the theoretical yields of butter and press cake from 100 pounds of average roasted nibs or liquor show the effect of different degrees of pressing. Assuming that the freshly roasted nibs contain 1.5 per cent of moisture and 53 per cent of fat, and that the press cakes contain 2 per cent of moisture, Table 1 gives the theoretical yields of butter and cake per 100 pounds of roasted nibs or liquor.

TABLE 1.—*Theoretical yields of cacao butter and cocoa cake per 100 pounds of nibs liquor*

[The theoretical loss of moisture amounts to 0.30 to 0.46 pound]

Degree of pressing (fat left in press cake)	Yield of cacao butter	Yield of press cake (moisture 2 per cent)
	Pounds	*Pounds*
Dry-pressed cake, containing 10 per cent fat	47.83	51.71
Dry-pressed cake, containing 13 per cent fat	46.04	53.53
Cake containing 15 per cent fat	44.78	54.82
Average low-grade cake, containing 17 per cent fat	43.45	56.17
"Breakfast cocoa" cake, containing 22 per cent fat	89.83	59.87

Of course, the yields of butter and press cake per 100 pounds of average raw beans yielding from 79 to 82 per cent of roasted nibs, would be from 79 to 82 per cent of the weights given in the table. These data all refer to butter and cake made from straight nibs.

The feasibility of increasing the yield of cacao butter, where this is the sole consideration, by pressing whole beans has been considered by at least one manufacturer. The following data furnished by him were obtained from a factory test on the pressing of "fair fermented" Accra beans. One hundred pounds of the raw beans yielded 81 pounds of roasted nibs containing, of course, some shells. The loss on roasting was about 5 pounds, leaving 14 pounds of shells, germs, fines, etc. From 218 pounds of the ordinary roasted nibs liquor 94 pounds of cacao butter and 124 pounds of cocoa press cake were obtained, or 43.12 pounds of butter and 56.88 pounds of cocoa press cake per 100 pounds of nibs. The material is stated to have been pressed for 40 minutes. From 228 pounds of liquor or mass resulting from grinding the roasted shells and germs fraction with the nibs 91.5 pounds of butter and 136.5 pounds of whole-bean cake were obtained—a butter yield of 47.07 pounds per 100 pounds of the nibs fraction present. The increased yield of butter is believed to have been due to the more fibrous and presumably more porous cake obtained from whole beans. Also the pressing time was 10 minutes longer than for the nibs test.[12]

The results of this isolated experiment, however, can hardly be interpreted as conclusively establishing the proposition that the yield of cacao butter is increased by pressing the whole beans.

DISPOSAL OF THE PRESS CAKE

Probably the most important factor in the disposal of low-grade cocoa cake and the one which determines the channels open for profitable disposal is the fat content of the product. Obviously it is the less well pressed, higher fat type of cake that is in demand by the concern engaged in recovering the fat through solvent extraction. This type of cake also is worth more as fuel than dry-pressed cocoa.

On the other hand, low-grade cocoa has been used as the raw material in the manufacture of theobromine, a valuable drug,[13] and for this use a high fat content in the cake is very undersirable. Theobromine and caffeine occur in the pressed cake in small quantities, usually to the extent of from 2 to 3 per cent, and the presence of much fat interferes with the extraction of these bases. The dry-pressed cake therefore commands a premium as raw material for this industry.

For use as fertilizer material, also, the less fat there is in a product, the better, as fats and oils not only have no plant-food value, but large quantities of oily substances are believed to be inimical to plant growth. Removal of fat from a given material also raises the percentage content of the other constituents; for example, removal of the fat from cocoa increases the percentage of nitrogen or "ammonia," potash, and phosphoric acid. Furthermore, fatty substances, when present in appreciable quantities, tend to lower the availability of the fertilizer constituents to growing plants, by coating the particles containing plant food with an impervious envelope and thus impeding their decomposition and solution.

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[12] The manufacturer who submitted these data remarks: "The speed of pressing seems to us to depend almost entirely on the strength of the filtering (press) pad used." The writers are not able to vouch for the general relevancy of this observation, however.

[13] Thousands of pounds of theobromine are used annually in the preparation of diuretics.

The proportion of the total by-product cake that has been directly consumed as fertilizer material is not accurately known. Statements obtained from producers and fertilizer men indicate that at least 3,000 tons have been sold for utilization as fertilizer within a year. If the cake that is subjected to solvent extraction for the recovery of the cacao fat, the residue from which finds its way into the fertilizer trade, be included also, probably at least one-fourth of the total quantity of by-product cake produced is eventually consumed as fertilizer.

Information as to the quantity of cake commercially extracted for recovery of the cacao fat was obtained; but inasmuch as only one establishment is engaged in this undertaking, the data can not be divulged.

Large quantities of low-grade cake have been burned under the manufacturers' boilers in the past; but the monetary value to be credited to the product from such disposal is small, and it is believed that only a few hundred tons were burned during 1924.

A small portion of the by-product cake produced has been consumed as raw material for the preparation of theobromine. As not more than two concerns are known to be using cocoa for this purpose, the exact quantity that is being used can not be stated.

Not less than 1,200 tons of the press cake was disposed of to mixed-feed manufacturers during 1924, and there are reasons for believing that the quantity of cocoa cake consumed in feeding stuffs for animals is on the increase.

The definite figures on which the foregoing estimates are based account for only about one-half of the by-product cocoa cake produced annually. As all of the known outlets for the cake of any commercial significance have been mentioned, however, it seems likely that the balance must have been disposed of through the same channels, or wasted outright.[14] Attempts have been made, so far without any great success, to market some of the better grade of surplus cake as an ingredient of bakery goods. Cocoa bread and wafers have been produced, but the tonnage of cocoa consumed in this way is negligible.

It has been suggested that certain manufacturers have endeavored to market pulverized low-fat cake as powdered cocoa for human consumption. This is beside the point, however, as the present study is concerned with the material held so cheaply by the producer as to give it a market value placing it within reach of the fertilizer trade.

COMPOSITION AND PROPERTIES

The literature of cacao contains much information on the composition and nature of cocoa from the viewpoint of its use as a beverage and food; but, with the exception of reports on the experimental feeding of the meal to dairy cattle, nothing has been found bearing specifically on the problem of the utilization of surplus or low-grade cocoa for other purposes. Such standard texts on cacao as those of Zipperer (*61*), Fritsch (*16*), van Hall (*19*), Whymper (*58*), and Knapp (*26*, *27*) make no mention of the use of the pressed cake for any purpose other than for the preparation of cocoa for human consumption, although they discuss the utilization of cacao shells in various ways.

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[14] Information to the effect that some low-fat cocoa cake and powder is shipped to northern Europe was volunteered by the warehouse manager of a Norfolk, Va., brokerage firm that had dealt largely in cocoa by-products, but the writers have been unable to confirm this statement.

A few tests of the value of cocoa meal, or ground cake, as food for cattle have been made in Europe. Pott (*36, p. 136–141*) mentions work with a mixture of "defatted cocoa meal with ground shells." The material was of variable composition, containing from 8 to over 16 per cent of fat, and from 2.54 to 3.33 per cent of nitrogen approximately equivalent to 16 to 21 per cent of crude protein. The figures for crude fiber and for ash are relatively high. It is stated that the product resembled palm-oil cake, and laboratory tests indicated that it was not readily digestible. Pott reports also that good results were obtained by feeding calves "cooked and partially defatted cacao husks." The analysis given for this material is evidence that it was a mixture of cake and shells. Stutzer's researches on the character of the nitrogenous substances in commercial cocoas are cited by Pott. This work by Stutzer (*47*) indirectly throws a little light on the possible value of ground cocoa cake as fertilizer, in that the amounts of total and water-soluble nitrogen and phosphoric acid are reported. In the case of a sample of pure cocoa powder, 21½ per cent of the nitrogen was found to be soluble in cold water, while 77 per cent of the total phosphoric acid found in the ash was water-soluble after incineration.[15]

Two extensive tests of the feeding value of cocoa cake for dairy cows have been reported in the literature. The first of these, a series of feeding experiments lasting more than two years, was conducted in Denmark by Lund (*30*). Two lots of dairy cows were used in the test, one lot receiving cocoa cake regularly. The maximum quantity of cake fed per cow per day was 2.42 pounds. The cows receiving cocoa cake gave less milk than the control animals. The results of additional experiments with laboratory animals appear to have led to the conclusion that, because of the poisonous properties of the theobromine and caffeine it contains, cocoa cake should not be used as cattle food.

Ellenberger and Newlander, of the Vermont Agricultural Experiment Station, have recently published a report of similar trials of feeding ground cocoa cake to dairy cows (*14*). The experiments "were planned simply to determine what would happen to dairy cattle when 10, 20, or more per cent of their daily ration[16] was made up of cocoa meal." The ground cocoa cake used in the trials was of the ordinary, higher-fat type, and as to composition would have satisfied the requirements for potable cocoa. Containing 21.14 per cent of crude fat, it fell just short of the qualifications for "breakfast cocoa." Its content of theobromine and caffeine was not considered.

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[15] Beythien and Pannwitz (*6*) report only 31 to 34 per cent of the total phosphoric acid in the ash of cacao beans as being soluble in water.

[16] The ration here meant was the daily grain or concentrate ration, not the total daily feed.

In these trials it was found that the cows readily ate a concentrate ration containing up to 1.18 pounds of cocoa meal per cow, per day, "with no apparent ill effect on their physical well-being." The feeding of cocoa to the extent of 20 per cent of the grain ration reduced the milk flow by as much as 13 per cent, but tended to increase the percentage of butterfat in the milk. One cow, a 476-pound Jersey heifer, is stated to have received a liberal grain ration containing up to 40 per cent of cocoa meal (averaging 1.75 pounds of the cocoa per day) for five and one-half months. During this period she gained 100 pounds, but her milk yield was greatly decreased. Several full-grown cows received as much as 2.2 pounds of cocoa meal per day each for periods of from one to three days. No mention is made of any untoward physiological symptoms that might be referable to theobromine, nor is the presence of this drug in the cocoa meal discussed.

Notwithstanding this apparent tolerance of cocoa by neat cattle, on the whole it must be concluded that caution should be observed in feeding cocoa products to animals. It can hardly be questioned that the quantity of cocoa that can be fed daily is limited; and, judging by reports of past experiences with the feeding of cacao shells, certain animals, notably horses, are especially susceptible to the poisonous action of theobromine.[17]

The extraction and preparation of theobromine commercially from cocoa cake does not appear to have been described in textbooks on the cocoa industry. Knapp (*26*), however, mentions a process patented by de Grousseau and Vicongne for the preparation of theobromine from cacao waste (*18*).

Utilization of by-product or surplus cocoa cake as fertilizer material has not previously received scientific consideration, a search of the literature reveals. Apparently not even laboratory investigation of the fertilizer possibilities of the product has ever been made. Though a few representatives of the fertilizer trade are familiar with the amounts of total "ammonia" and potash present in the cakes and extracted cocoa, no information appears to have been published or made available on the solubility or quality of the ammonia or on the range in fat content. Neither has the theobromine content and general nature of the extracted cocoa been investigated. It was deemed necessary, therefore, to obtain authentic samples of the different types of cocoa by-products and to undertake a laboratory study of their chemical composition and nature.

PRESENT INVESTIGATION

Samples representative of the by-product cocoa cake and of the solvent-extracted cocoa being produced in the United States were requested from manufacturers. Eighteen samples were obtained, of which 12 were hydraulically pressed cake and 4 represented defatted cocoas that had been subjected to solvent extraction. One of the cakes was made by pressing ground whole beans, including shells and germs. Two samples of commercial cacao shells also were obtained. Five producers of by-product press cake and the one firm engaged commercially in extracting cacao fat with a solvent, sent in samples.

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[17] One producer of the by-product cake stated that his attention had been called to a case in which the death of a number of hogs was attributed to feeding them cocoa meal.

Certain analytical data, usually not considered by the fertilizer chemist, such as the contents of crude fiber and alkaloids, and the calorific value, have been determined on a number of the samples, because it was recognized that utilization of cocoa by-products as fertilizer material is in competition with their use as fuel, as feed stuff, and as a source of theobromine.

The samples were ground to pass a 40-mesh sieve preparatory to the chemical examination. The methods of chemical analysis of the Association of Official Agricultural Chemists (*3*) were followed except as hereinafter noted.

Total organic and ammoniacal nitrogen was determined by the Kjeldahl-Gunning-Arnold method in the nitrogen section of the Bureau of Chemistry. The determination of theobromine plus caffeine was made in the drug control and pharmacognosy laboratories of the Bureau of Chemistry by a method worked out in those laboratories. Features of this method are: (1) Suspension of the cocoa material in weakly acidified water, and extraction of the alkaloids with chloroform in a special continuous-extraction apparatus; (2) purification of the extracted alkaloids by sublimation. It was found that higher yields of the alkaloids were obtained by this method than by the one-time official Dekker-Kunze method (*51, p. 254–255*); and the theobromine and caffeine recovered were of high purity. It was considered unnecessary to determine the bases separately, as the caffeine is known to amount to only about 5 per cent of the total alkaloid content.

The examinations relating to fuel value, involving determinations of moisture, volatile matter, ash, fixed carbon (by difference), sulphur, and calorific value, were made on other subsamples, in the coal analysis laboratory of the United States Bureau of Mines.[18]

In both the ether and petroleum-ether extractions it was found to be necessary to mix asbestos with the charges of material to render them more permeable to the solvent. The asbestos was first washed and ignited and its only effect on the determinations was to insure complete extraction.

The method used in determining crude fiber differed from the one adopted as official for cacao products, in that purified and ignited asbestos was added to the charge to facilitate filtration; and linen, and asbestos felt in a Gooch crucible, were used as the filtering mediums after the acid and alkali digestions, respectively.

Table 2 contains the analytical data obtained for the cocoa press cakes, including the sample of "whole bean" cake.[19] The results of the chemical investigation of the solubility and quality (or so-called availability) of the nitrogen of the press cakes, extracted cocoas, and cacao shells, are presented in Table 3 (p. 20). Table 4 (p. 30) contains the results of the analyses of the solvent-extracted cocoas; and Table 5 (p. 37) shows the composition of the two samples of cacao shells.

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[18] These determinations were made by H. M. Cooper. The results have been correlated with the moisture and ash data obtained on the original samples in this laboratory.

[19] Check determinations for a number of the results were made by F. O. Lundstrom and R. M. Jones, assistant chemists, and W. O. Robinson, associate chemist, Bureau of Soils; and M. R. Coe, assistant chemist, Bureau of Chemistry.

TABLE 2.—*Composition and fuel value of by-product cocoa press cake*

Sample		Material as received										
Number	Description	Moisture	Ether extract (crude fat)	Petroleum ether extract	Nitrogen (total) expressed as ammonia, NH_3	Phosphoric acid (total) expressed as P_2O_5	Potash (total) expressed as K_2O	Ash	Crude fiber	Theobromine and caffeine alkaloids	Fuel value data [1]	
											Calorific value per kilogram	Volatile matter
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Kgm.-cal.*	*Per cent*
5108	Ordinary (produced in 1922)	5.00	18.40	(3)	4.89	1.65	1.88	4.95	5.45	[4] 2.15	(3)	(3)
5618	Ordinary, high in fat	3.49	24.35	23.20	4.52	1.44	2.13	6.26	5.23	(3)	(3)	(3)
102	Ordinary, high in fat (from Accra beans)	2.00	21.56	20.85	4.69	1.03	1.71	5.03	5.15	(3)	5,499	75.3
103	Dry-pressed [6]	2.09	15.19	14.74	4.45	1.18	2.29	6.52	8.05	(3)	(3)	(3)
104	Dry-pressed [6]	2.69	14.83	14.63	4.83	1.34	1.75	5.72	5.81	(3)	(3)	(3))
105	Ordinary, sold for fat extraction	4.92	16.68	15.50	4.67	1.24	1.83	5.62	5.75	2.70	5,108	70.7
108	Ordinary (from Accra beans)	3.02	19.52	18.59	4.64	1.34	1.70	5.13	5.30	2.80	(3)	(3)
110	Dry-pressed (From Sanchez beans)	4.35	10.65	9.45	5.44	2.26	2.15	6.30	4.81	(3)	4,799	68.8
111	Dry-pressed (From Accra beans)	3.78	9.26	8.17	5.35	1.86	1.79	7.16	5.81	3.20	4,901	68.6
113	Ordinary (from Accra beans) [7]	2.17	19.05	18.66	4.75	1.26	2.08	5.31	6.05	(3)	(3)	(3)
114	"Whole bean" cake (from Accra beans) [7]	2.11	14.19	13.69	4.77	1.31	2.30	5.98	8.06	(3)	(3)	(3)
109	Dry-pressed, from miscellaneous cocoa wastes, including "fines"	4.71	13.62	12.29	4.28	1.35	2.59	8.35	8.54	(3)	(3)	(3)
	Average, ordinary type cake (6 samples)	3.43	19.93	[8] 19.36	4.69	1.33	1.89	5.38	5.49	[9] 2.75	[9] 5,304	[9] 73.0
	Average, dry-pressed type cake (4 samples) [10]	3.23	12.48	11.75	5.02	1.66	2.00	6.43	6.12	[11] 3.20	[9] 4,850	[9] 68.7
	Average pressed cake (10 samples) [10]	**3.35**	**16.95**	[12] **15.98**	**4.82**	**1.46**	**1.93**	**5.80**	**5.74**	[13] **2.90**	[14] **5,077**	[14] **70.9**

Sample		On dry, ether-extract-free basis						Ether extract, volatile matter, and fuel value on dry, ash-free basis [1]			
Number	Description	Nitrogen (total) expressed as ammonia, NH_3	Phosphoric acid (total) expressed as P_2O_5	Potash (total) expressed as K_2O	Ash	Crude fiber	Theobromine and caffeine alkaloids	Ether-extract (crude fat)	Volatile matter	Calorific value, per kilogram	Calorific value of nonfatty organic matter for each per cent per kilogram [2]
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Kgm.-cal.*	*Kgm.-cal.*
5108	Ordinary (produced in 1922)	6. 38	2. 15	2. 45	6. 46	7. 11	[4] 2. 81	(5)	(5)	(5)	(5)
5618	Ordinary, high in fat	6. 26	2. 00	2. 95	8. 68	7. 25	(3)	(5)	(5)	(5)	(5)
102	Ordinary, high in fat (from Accra beans)	6. 14	1. 35	2. 24	6. 58	6. 74	(3)	23. 19	81. 0	5, 915	48. 9
103	Dry-pressed [6]	5. 38	1. 43	2. 77	7. 88	9. 73	(3)	(5)	(5)	(5)	(5)
104	Dry-pressed [6]	5. 86	1. 62	2. 12	6. 94	7. 04	(3)	(5)	(5)	(5)	(5)
105	Ordinary, sold for fat extraction	5. 96	1. 58	2. 33	7. 17	7. 33	3. 44	18. 65	79. 0	5, 710	48. 9
108	Ordinary (from Accra beans)	5. 99	1. 73	2. 19	6. 62	6. 84	3. 61	(5)	(5)	(5)	(5)
110	Dry-pressed (from Sanchez beans)	6. 40	2. 66	2. 53	7. 41	5. 66	(3)	11. 92	77. 0	5, 371	48. 4
111	Dry-pressed (from Accra beans)	6. 15	2. 14	2. 06	8. 23	6. 68	3. 68	10. 40	77. 0	5, 503	50. 6
113	Ordinary (from Accra beans) [7]	6. 03	1. 60	2. 64	6. 74	7. 68	(3)	(5)	(5)	(5)	(5)
114	"Whole bean" cake (from Accra beans) [7]	5. 70	1. 57	2. 75	7. 14	9. 63	(3)	(5)	(5)	(5)	(5)
109	Dry-pressed, from miscellaneous cocoa wastes, including "fines"	5. 24	1. 65	3. 17	10. 22	10. 46	(3)	(5)	(5)	(5)	(5)
	Average, ordinary type cake (6 samples)	6. 13	1. 74	2. 47	7. 04	7. 16	[9] 3. 53	[9] 20. 92	[9] 80. 0	[9] 5, 813	[9] 48. 9
	Average, dry-pressed type cake (4 samples) [10]	5. 95	1. 96	2. 37	7. 62	7. 28	[11] 3. 68	[9] 11. 16	[9] 77. 0	[9] 5, 437	[9] 49. 5
	Average pressed cake (10 samples) [10]	**6. 06**	**1. 83**	**2. 43**	**7. 27**	**7. 21**	[13] **3. 58**	[14] **16. 04**	[14] **78. 5**	[14] **5, 625**	[14] **49. 2**

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[1] The determinations of calorific value and volatile matter were made by H. M. Cooper, United States Bureau of Mines, on moisture-free samples. In this table his results have been correlated with the moisture and ash figures obtained on the original samples by the authors.

[2] The calorific value accepted for the ethyl-ether extract is 93 kgm.-cal. for each per cent per kilogram (9,300 Cal. per kilogram).

[3] Not determined.

[4] Reported as "theobromine," only, and not included in the averages. This determination was made in the food control laboratory, Bureau of Chemistry. Other work on cocoa has indicated that caffeine forms about 5 per cent of the total alkaloid in cacao products.

[5] Fuel value not determined.

[6] The manufacturer designated samples 103 and 104 "average run" and "highest grade," respectively, but these descriptions refer only to his "dry-pressed" cake; sample 103 is low-grade pressed cake.

[7] Samples 113 and 114 are by-product cakes made from the same lot of "fair fermented," roasted Accra beans, with the ordinary type of pressing equipment; but 113 is nibs by-product cake, while 114 was made from the whole beans.

[8] Five samples.

[9] Two samples.

[10] The data for samples 109 and 114 were omitted in obtaining the averages, since these samples differed from straight by-product cake in containing important amounts of shells and miscellaneous materials.

[11] One sample.

[12] Nine samples.

[13] Three samples.

[14] Four samples.

The four samples of press cake numbered 105, 109, 110, and 111 (Tables 2 and 3) represent three distinct commercial types of pressed cocoa residues. The last three were produced by one of the largest manufacturers of cacao butter, and are examples of dry-pressed cakes. Sample No. 105 is typical of ordinary by-product cocoa of average fat content, and represents a lot of cake that had been purchased for the recovery of its fat by solvent extraction. Number 109 is a composite of dry-pressed cakes resulting from the pressing of accumulated fines containing cacao germs. The high content of ash and of crude fiber mark this sample as including some shell material and probably cocoa dust and sweepings. Inclusion of the germs tended to increase the nitrogen content of this sample of low-grade material. Cacao germs separated from roasted beans and analyzed by Richards (*37*), had a nitrogen content of 5.5 per cent, equivalent to 6.7 per cent of ammonia. Samples 110 and 111 are excellent examples of the dry-pressed, straight nibs, by-product cocoa. No. 110 is stated to have been made from Sanchez (San Domingo) beans, whereas No. 111 was made from "almost straight run" Accra (Gold Coast, West Africa) beans. Both of these varieties of cacao are classed by van Hall (*19*) as among the lowest priced and most ordinary sorts, considered from the point of view of the flavor and quality of the chocolate produced from them.

Accra beans particularly, however, are well suited to the needs of the manufacturer primarily after a large yield of cacao butter, as both the proportion of nibs and the fat content of the nibs are relatively high (*58, p. 112*). The imports of beans from British West Africa, largely Accra, amounted to more than one-third of all cacao brought into the United States in 1923 (*53, Table 3*).

Samples 113 and 114 were submitted by a manufacturer as representing, respectively, the nibs cake and the whole bean cake produced in the factory test pressing, mentioned on page 9. This experiment, which was designed to compare the yield of cacao butter from ordinary nibs with that obtained by pressing all parts of the bean together, showed an increased production amounting to 4 pounds of butter (per 100 pounds of roasted nibs fraction), when the ground nibs, shells, and germs were pressed together. Both the separated nibs, from which sample 113 was produced, and the manipulated whole beans, of which sample 114 represents the press cake, were from the same lot of "fair fermented" and roasted Accra cacao.

Unfortunately, however, these samples can not be considered representative as to fat content of the respective cakes. No. 113 consisted of two chunks from the outside edge of the nibs press cake, and No. 114 was a single piece from the interior of the whole-bean cake. As the periphery of any hydraulically pressed oil cake is richer in oil or fat than the interior portions of the cake, and as cocoa press cakes are disk-shaped, only a sample consisting of a perfect sector could have been representative as to fat content of either cocoa cake.[20] Nevertheless, the decidedly higher percentage of fat found in sample 113 as compared with sample 114 (Table 2),[21] indicates at least that this manufacturer was able to press the whole beans to a drier cake than when pressing the separated nibs alone. The fact that these samples were not representative as to fat content does not affect the validity of the other analytical results calculated to the dry, ether-extract-free basis, for these two press cakes. If the data furnished on the yields of cacao butter and cake be accepted, and an average shell content of 12 per cent of the whole roasted beans be assumed, the whole-bean cake represented by sample 114 must have contained 20 per cent of pure shell matter.

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[20] Sectors taken from top, middle, and bottom cakes in the press would be required to give a representative sample of an entire pressing.

The solvent-extracted samples, for which the analytical results are given in Tables 3 and 4, are discussed in the section devoted to the extracted cocoas on page 29.

The amount of substance soluble in ethyl ether, designated ether extract in the tables, is commonly taken as the measure of the crude fat content of a sample. This applies particularly to materials used as feed stuffs. For the cocoa samples the petroleum-ether extract was determined also, because for cacao beans and many oil-bearing seeds this more nearly approximates the true fat than does the ethyl-ether extract (compare Dubois (*12*), *p. 161*).

In fact, in the cocoa industry, the amount of extract obtained with light petroleum ether has come to be accepted as the fat content for cacao products.[22]

The ash and crude fiber results are of significance in attempting to estimate the amount of impurities and shell material present in a cocoa cake. Food Inspection Decision 191 (*52*), issued by this department, in defining "cocoa," or "powdered cocoa," restricts the use of these terms to cocoa that contains, on the moisture and fat-free basis, not more than 8 per cent of total ash, not more than 0.4 per cent of ash insoluble in hydrochloric acid, and not more than 7 per cent of crude fiber.[23] On this basis alone, it can be seen that samples 102, 108, and 110 satisfy the total ash and fiber requirements for edible cocoa, whereas 5108, 104, and 111 are nearly within the limits. Sample No. 5618, with its 23.20 per cent of cacao fat, is not far from qualifying as breakfast cocoa, being only a fraction of 1 per cent too high in total ash and crude fiber. All the samples included in Table 2, however, are supposed to represent only by-product cocoa cakes.

The calorific values of the four press cakes examined range from 4,799 to 5,499 Calories per kilogram, or 8,638 to 9,898 British thermal units per pound. Anthracite coal of ordinary good grade may be assumed to have an average calorific value of 7,200 Calories per kilogram, or nearly 13,000 British thermal units per pound; the corresponding values for average bituminous coal of good grade are 7,800 Calories per kilogram, or about 14,000 British thermal units per pound. The average fuel value found for the cocoa cakes is therefore, on paper, 70 per cent of the fuel value of anthracite and about two-thirds that of bituminous coal.

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[21] Accepting the yield data furnished by the manufacturer and assuming normal values for the composition of the whole roasted beans (pure nib 87.2 per cent, containing 54 per cent of fat; shell 12 per cent, containing 4 per cent of fat; germ 0.8 per cent, containing 3.6 per cent of fat), and the presence of 2 per cent of shells in the separated nibs fraction, the theoretical fat content of the nibs press cake represented by sample 113 should have been 17.4 per cent, and the whole-bean cake, from which sample 114 was taken, should have contained 12.5 per cent of fat. The crude fiber results on No. 113, however, indicate that the separated nibs contained more than 2 per cent of shells.

[22] Ethyl-ether extracts from cocoa an appreciable quantity of apparently nonfatty substance that does not occur in the petroleum-ether extract; and it is sometimes stated that the ethyl-ether extract contains any free or uncombined theobromine present in the cocoa. Wadsworth's data on the solubility of theobromine (*55*) show, however, that even if all of the theobromine in a 2-gram charge of a sample like No. 5108 were in the uncombined condition, in order for it to appear in the extract over 1,400 cubic centimeters of the ether would have to become saturated with theobromine in passing through the charge.

[23] A formula for calculating the quantity of shell material present in cocoa from the crude fiber content, has been published by Baker and Hulton (*5*): and more recently Taber (*48*) has further investigated the determination of shell content.

Volatile matter, reported in the tables, represents a value empirically determined by fuel chemists in the proximate analysis of coal and related products, and should not be confused with the "organic matter" of the general analyst. Except for the empiric features in its determination, volatile matter corresponds to total organic matter less fixed carbon. The sum of the percentages of moisture, volatile matter, fixed carbon, and ash equals 100. The volatile matter data proved to be of significance in indicating the degree of charring undergone by one of the samples of dried, solvent-extracted cocoa.

It is evident that the calorific value of the cocoa cakes increases with the fat content. Investigation of this relationship has brought out an interesting fact. If 9,300 Calories per kilogram be accepted as the heat of combustion or calorific value of cacao fat (*26, p. 166; 21, p. 44; 45,*) and this fuel value be assigned to the ethyl-ether extracts of the cocoa samples, a simple calculation serves to show that, on the moisture-free and ash-free basis, the nonfatty, organic substance of cocoa has a rather uniform heat of combustion of about 4,900 Calories per kilogram. With the exception of sample No. 107, known to have been partially charred in drying, the range is from 4,840 to 5,060 Calories.[24] It is therefore possible to approximate closely the total fuel value (heat of combustion) of a particular lot of cocoa, knowing merely its content of moisture, fat, and ash. It is believed that a value within a few per cent of the actual heat of combustion value will be given by the following formula:

$$C=44\ F+4{,}900-49\ (M+A).$$

C=the calorific value of the cocoa sample "as is"; that is, on the original moisture and ash content basis, expressed in Calories per kilogram.[25] M=the per cent of moisture in the sample. A=the per cent of ash in the sample. F=the per cent of crude fat or ethyl-ether extract in the sample.

If the content of petroleum-ether extract is taken as the measure of the fat; that is, if F is equal to the percentage of petroleum-ether extract in the sample, and assuming 9,300 Calories per kilogram to be the calorific value of the petroleum-ether extract, recalculation of the data yields the following formula:

$$C=43.2\ F+4{,}980-49.8\ (M+A).$$

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[24] This calorific value might hold for the nonfatty material of other oleaginous seeds or fruits. As data were available for a sample of olive pomace, the test was applied to this material. The sample was a very thoroughly pressed residue from the manufacture of olive oil, containing only 5.8 per cent of ether extract, on the moisture-free and ash-free basis. On this basis the nonfatty substance had a calorific value of 5,025 Calories per kilogram.

[25] To convert this value into B. t. u. per pound, multiply the Calories per kilogram by 1.8.

Sulphur to the extent of 0.2 to 0.3 per cent was found in the four press cakes examined as to fuel value.

The values reported for total nitrogen in Table 3 (for which ammonia equivalents are given in Tables 2, 4, and 5) are for total organic and ammoniacal nitrogen. These figures, however, may be accepted as representing the total nitrogen content, as the delicate diphenylamine test for nitrates showed hardly a trace of nitrate-nitrogen to be present in the cakes. "Ammonia" is the term commonly used in the fertilizer trade to cover the total nitrogen content of a product.

TABLE 3.—*Solubility and quality of the nitrogen in cocoa by-products*

Sample		Determined on material as received													Calculated to dry, ether-extract-free basis								
		Total nitrogen		Water-soluble nitrogen [1]		Water-insoluble nitrogen					Water-soluble plus "active" insoluble nitrogen				Total nitrogen		Water-soluble nitrogen [1]	Water-insoluble nitrogen			Water-soluble plus "active" insoluble nitrogen	
											As shown by the neutral permanganate method		As shown by the alkaline permanganate method									
Number	Description	N	Alkaloid nitrogen	In sample	As percentage of total nitrogen	Total in sample	Soluble in neutral permanganate solution	Distilled from alkaline permanganate solution	"Activity" by neutral permanganate, as percentage of water-insoluble nitrogen	"Activity" by alkaline permanganate, as percentage of water-insoluble nitrogen	In sample	As percentage of total nitrogen	In sample	As percentage of total nitrogen	N	Alkaloid nitrogen	Total soluble	Total insoluble	Soluble in neutral permanganate solution	Distilled from alkaline permanganate solution	By the neutral permanganate method	By the alkaline permanganate method
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
5618	Ordinary by-product press cake	3.72	------	1.53	41.1	2.19	1.36	0.49	62.1	22.4	2.89	77.7	2.02	54.3	5.16	------	2.12	3.04	1.88	0.68	4.00	2.80
102	Ordinary by-product press cake	3.86	------	1.51	39.1	2.35	1.26	.52	53.6	22.1	2.77	71.8	2.03	52.6	5.05	------	1.98	3.07	1.65	.68	3.63	2.66
103	Dry-pressed cake	3.66	------	1.32	36.1	2.34	1.27	.46	54.3	19.7	2.59	70.8	1.78	48.6	4.43	------	1.60	2.83	1.53	.55	3.13	2.15
104	Dry-pressed cake	3.97	------	1.44	36.3	2.53	1.17	.48	46.2	19.0	2.61	65.7	1.92	48.4	4.81	------	1.74	3.07	1.42	.58	3.16	2.32
105	Ordinary by-product press cake	3.84	0.79	1.40	36.5	2.44	1.36	.51	55.7	20.9	2.76	71.9	1.91	49.7	4.90	1.01	1.79	3.11	1.73	.65	3.52	2.44
108	Ordinary by-product press cake	3.82	.82	1.49	39.0	2.33	1.10	.51	47.2	21.9	2.59	67.8	2.00	52.4	4.93	1.06	1.92	3.01	1.42	.66	3.34	2.58
110	Dry-pressed cake from Sanchez beans	4.47	------	1.54	34.5	2.93	2.05	.69	70.0	23.5	3.59	80.3	2.23	49.9	5.26	------	1.81	3.45	2.41	.81	4.22	2.62
111	Dry-pressed cake from Accra beans	4.40	.94	1.63	37.0	2.77	1.97	.63	71.1	22.7	3.60	81.8	2.26	51.4	5.06	1.08	1.87	3.19	2.27	.73	4.14	2.60
109	Dry-pressed miscellaneous cocoa wastes	3.52	------	1.15	32.7	2.37	.93	.45	39.2	19.0	2.08	59.1	1.60	45.5	4.31	------	1.41	2.90	1.14	.55	2.55	1.96
101	Solvent-extracted cocoa	4.20	------	1.87	44.5	2.33	1.14	.52	48.9	22.3	3.01	71.7	2.39	56.9	4.73	------	2.11	2.62	1.28	.58	3.39	2.69
106-A	Solvent-extracted cocoa, dried at 100° C	4.42	------	1.56	[3] 35.3	2.86	1.37	.60	47.9	21.0	2.93	66.3	2.16	48.9	4.81	------	1.70	3.11	1.49	.65	3.91	2.35

107	Commercial solvent-extracted cocoa, somewhat charred	4.39	------	1.43	32.6	2.96	1.04	.57	35.1	19.3	2.47	56.3	2.00	45.6	4.87	------	1.59	3.28	1.15	.63	2.74	2.22
116	Commercial solvent-extracted cocoa, but less charred in drying	4.45	.94	1.63	36.6	2.82	1.48	.48	52.5	17.0	3.11	69.9	2.11	47.4	4.86	1.03	1.78	3.08	1.62	.52	3.40	2.30
115	Commercial cocoa shells	2.97	.59	1.18	39.7	1.79	.82	.27	45.8	15.1	2.00	67.3	1.45	48.8	3.38	.67	1.34	2.04	.93	.31	2.27	1.65
117	Commercial cocoa-shell meal	2.74	.47	.81	29.6	1.93	.76	.37	39.4	19.2	1.57	57.3	1.18	43.1	3.21	.55	.95	2.26	.89	.43	1.84	1.38
	Average by-product press cake (8 samples) [2]	**3.97**	[4] .85	1.48	**37.3**	2.49	1.44	.54	**57.8**	**21.7**	2.92	73.6	2.02	50.9	4.95	[4] 1.05	1.85	3.10	1.79	.67	3.64	2.52
	Average solvent-extracted cocoa (4 samples)	**4.36**	[5] .94	1.62	**37.2**	2.74	1.26	.54	**46.0**	**19.7**	2.88	66.1	2.16	49.5	4.82	[5] 1.03	1.80	3.02	1.38	.59	3.18	2.39
	Average commercial cocoa shells (2 samples)	**2.86**	.53	1.00	**35.0**	1.86	.79	.32	**42.5**	**17.2**	1.79	62.6	1.32	46.2	3.30	.61	1.15	2.15	.91	.37	2.06	1.52

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[1] Practically all of the theobromine and caffeine in the samples examined was found to be soluble in water at room temperature; hence the alkaloid nitrogen is included in the water-soluble nitrogen, of which it apparently constitutes 50 to 60 per cent. The Kjeldahl method is reported to recover less than 95 per cent of the nitrogen in theobromine. The caffeine nitrogen amounts to about 5 per cent of the total alkaloid nitrogen.

[2] The data for sample 109 were not included in the averages.

[3] Determinations of water-soluble nitrogen, made directly on the original wet sludge, showed only 27.7 per cent of the total nitrogen to be soluble. After drying in the laboratory at 100° C. the solubility was found to be 35.3 per cent.

[4] Three samples.

[5] One sample.

"Ammonia" designates the amount of ammonia (NH_3) equivalent to the total nitrogen present, and its percentage is obtained by multiplying the percentage of total nitrogen by 1.2159. Crude protein (sometimes stated merely as protein), of significance in the animal-feeding world, also is a concept related to the nitrogen content. The percentage of crude protein is obtained by multiplying the percentage of total organic and ammoniacal nitrogen by the arbitrary factor 6.25. The crude protein content of the cocoa cakes, omitting samples 109 and 114, therefore varies from 22.38 to 27.94 per cent and averages 24.8 per cent, or 31.1 per cent on the dry, ether-extract-free basis.

In order properly to understand and interpret the data contained in Table 3, on the solubility and quality of the nitrogen of the cocoa samples, it is necessary to know just what the *neutral* and *alkaline* permanganate tests are intended to show. These tests are based on two independent purely chemical methods of procedure designed to distinguish fertilizer materials whose water-insoluble "organic nitrogen" is relatively inert or resistant to decomposition in the soil and slowly becomes available to growing plants, from materials whose water-insoluble "organic nitrogen" quickly decomposes in the soil, yielding compounds that are readily assimilated by plants. The two methods have been developed by different groups of chemists of the State experiment stations, and it happens that the alkaline permanganate test is more generally used in New England and the Middle Atlantic States, while the neutral permanganate method is the one in vogue in the South.

It is no longer claimed by their respective proponents that either method is quantitative in the sense of determining the actual percentage of the insoluble nitrogen that is available to plants (*23*, *46*). The tests are credited, however, with being means of distinguishing in a qualitative way between good and poor sources of water-insoluble organic nitrogen by showing the relative lability of the nitrogenous compounds, or the so-called *activity* of such nitrogen.

For mixed fertilizers, by common consent, arbitrary limits have been established for the percentage activity of the water-insoluble nitrogen below which this insoluble nitrogen is held to be of inferior quality. By percentage activity is meant the percentage of the water-insoluble nitrogen shown to be active by the particular permanganate test being used. The limit is different for each of the two tests. At its 1924 convention, the Association of Official Agricultural Chemists (*20*) adopted the following as tentatively official:

> The water-insoluble nitrogen in mixed fertilizers showing activity below 50 per cent by the alkaline method and below 80 per cent by the neutral method shall be classed as inferior.

Such official limits have not been fixed for defining an acceptable activity for water-insoluble nitrogen in the crude or unmixed fertilizer materials furnishing organic nitrogen. An activity of 50 or 55 per cent by the alkaline method is commonly considered to be the passing mark, however, for the insoluble nitrogen of unmixed materials, furnishing organic nitrogen; whereas, in the neutral permanganate test, if any dividing line were generally adopted, it probably would not be far from 80 per cent activity (*39*). From Table 3 it will be seen that, on the basis of its activity by either permanganate method, the water-insoluble nitrogen of the cocoa products must be classed as of inferior quality.

On the other hand, for organic materials, the cocoa products contain a relatively large share of their total nitrogen in a form soluble in water. Indeed, the press cakes and extracted cocoas contain a greater actual amount of water-soluble nitrogen than has been reported for typical samples of such standard organic ammoniates as cottonseed meal and castor-bean pomace (*23*). Such water-soluble organic nitrogen, in recognized fertilizer materials, is generally conceded to be highly available to growing plants.[26]

In the cocoa products, however, the water-soluble nitrogen includes the alkaloid nitrogen, since practically all (94 to 99 per cent) of the theobromine and caffeine was found to be readily extracted by water at room temperature; and this alkaloid nitrogen probably has no plant-food value.

The total amount of alkaloid nitrogen present in the samples examined ranges from 0.5 per cent for one of the cocoa shell samples to 1 per cent in samples of press cake and extracted cocoa. Of this, the Kjeldahl method is reported to recover, at best, less than 95 per cent (*56*). Table 3 includes the calculated amounts of alkaloid nitrogen that would be obtained by the method used in the nitrogen determinations, for the samples assayed for theobromine and caffeine; and it will be seen that the alkaloid nitrogen constitutes 50 to 60 per cent of the water-soluble nitrogen.

Theobromine and caffeine in the pure, uncombined state have been found to be toxic to certain plants in water cultures, and the significance of this is discussed on page 25.

The sum of the amounts of water-soluble and active insoluble organic nitrogen (as determined by either permanganate method), commonly loosely termed the available nitrogen, is often used as a basis for judging the quality or fertilizer value of crude ammoniates intended for use as a source of organic nitrogen. A regulation at one time in force in several of the Southern States required "that in unmixed fertilizing materials furnishing organic nitrogen, the sum of the water-soluble organic nitrogen and the permanganate soluble part of the water-insoluble organic nitrogen [as determined by the neutral permanganate method] shall amount to 85 per cent of the total organic nitrogen" (*7*). Though the cocoa products do not meet this requirement, it is interesting to compare the quality of their nitrogen as indicated by the alkaline permanganate test with data obtained by the same method by Jones on the nitrogen of cottonseed meal and castor-bean pomace.

In a sample of very high-grade cottonseed meal containing 7.02 per cent of total nitrogen, Jones (*23*) found 0.63 per cent of water-soluble nitrogen (less than 9 per cent of the total), and 4.09 per cent of active insoluble nitrogen. The so-called available nitrogen amounted, therefore, to 4.72 per cent, or 67 per cent of the total nitrogen. The sample of castor pomace examined by Jones contained 5.28 per cent of total nitrogen, of which less than 17 per cent was water-soluble and 65 per cent was available. The water-soluble nitrogen amounted to 0.88 per cent, and the active insoluble to 2.55 per cent, making the total so-called available nitrogen 3.43 per cent. From Table 3 it may be seen that for the cocoa cakes the water-soluble plus active insoluble, or so-called available nitrogen, as determined by the alkaline permanganate method, ranges from 1.78 to 2.26 per cent, and for the solvent-extracted cocoas from 2.00 to 2.39 per cent. These values amount to from 46 to 57 per cent of the total nitrogen.

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[26] The availability of water-soluble organic nitrogen is commonly accepted (*23*), but recently Robinson has pointed out that this has not been proved by experimental investigation (*39*).

If, however, the average alkaloid nitrogen percentages determined (0.85 per cent for the press cakes and 0.94 per cent for the extracted cocoa) be deducted on the grounds that the alkaloid nitrogen can not be classed as available, the nitrogen availability percentages are greatly reduced. Similarly, the water-soluble plus active, or total soluble nitrogen as determined by the neutral permanganate method in the pressed and the extracted cocoas amounts to 2.47 to 3.60 per cent of the material, but after deducting the presumably valueless alkaloid nitrogen, the range becomes 1.53 to 2.75 per cent for the soluble nonalkaloid nitrogen.

One reason for discounting the value of the soluble alkaloid nitrogen is the fact that experiments have been reported showing theobromine and caffeine to have injured certain plants in water or sand cultures. The significance of this is discussed below. But even if it could be shown that in the soil these alkaloids were not especially harmful to plants, the work of Robinson, Winter, and Miller on the effects of alkaline permanganate on various organic compounds containing amino- and imino-nitrogen (*38*), suggests that the alkaloid nitrogen may be so linked in the alkaloid molecule as to be somewhat resistant to conversion into forms that are available to growing plants.

Some idea of the relative fertilizer value of the cocoa products may be obtained by comparing their contents of plant-food constituents, total "ammonia," phosphoric acid, and potash, as shown in Table 2 (p. 14), with the quantities of these plant nutrients in seed residues of a similar nature. The average ammonia content of 72 samples of commercial castor-bean pomace, examined at the Connecticut Agricultural Experiment Station in 1923, was 6.2 per cent; and it is stated that this material usually contains about 2 per cent of phosphoric acid and 1 per cent of potash (*4*). The cocoa cakes, then, contain on the average about three-fourths as much total "ammonia" and phosphoric acid and twice as much potash as ordinary commercial castor pomace. The by-product cocoas more nearly resemble commercial cottonseed feed in plant-food content, however, than they do any other material whose fertilizer analysis has been found. Henry and Morrison (*21*) report that the average nitrogen content of 406 samples of cottonseed feed was 3.92 per cent. This is equivalent to 4.77 per cent of ammonia. The percentages of phosphoric acid and potash in cottonseed feed are given as 1.47 per cent each, so the contents of the principal plant-food constituents of average cottonseed feed agree rather closely with the corresponding figures for the cocoa press cakes examined.

The amount of plant-food elements present in the straight cocoa-nibs cakes, in general, will vary inversely with the amount of fat present. This is borne out by the data for total ammonia in Table 2.

If No. 109, the sample of pressed fines, and No. 103, which the ash and fiber results indicate is not a straight nibs cake, be excluded, it will be seen that the ammonia content of the samples on the dry, fat-free basis is fairly uniform, varying only from 5.86 to 6.40 per cent.

The data on the quantities of the various forms of nitrogen have been calculated to the moisture-free, ether-extract-free basis also, and these values are shown in Table 3.[27]

The quantities of theobromine and caffeine found in the cocoa products examined (Tables 2, 4, and 5) are above the averages reported in the literature for powdered cocoas and cocoa shells by such recent investigators as Knapp (*26*) and Wadsworth (*57*). The use of special apparatus for continuous chloroform extraction of the samples while in aqueous suspension, made possible a very thorough extraction of the alkaloids.

Although the theobromine and caffeine content, because of the toxicity of these bases, is of the greatest importance in relation to utilization of the cacao products as feedstuffs, the amount of these alkaloids present may also be significant if the material is to be used as fertilizer. Schreiner and Skinner (*41, p. 72, 78*) have interpreted work by Lutz (*31*) indicating caffeine to be harmful in sand cultures to maize and species of Cucurbita, and later experiments by Molliard (*34*) which showed both caffeine and theobromine to be harmful in water cultures to radishes. On the other hand, ricin (an active constituent of the castor bean) was found to be harmful to wheat seedlings in water cultures (*41, p. 78*); but the presence of this constituent does not appear to have been prejudicial to the general use of castor pomace as fertilizer material.

The Kjeldahl method for the determination of nitrogen recovers as ammonia nearly 36 per cent of the weight of theobromine present (*56*); hence it is apparent that out of the total "ammonia" content of the cocoa products examined for theobromine plus caffeine (Tables 2, 4, and 5), from 0.96 to 1.14 per cent ammonia in the press cakes, 1.14 per cent in the sample of extracted cocoa examined, and 0.57 to 0.71 per cent in the shells, must be derived from the alkaloidal bases. To repeat, this ammonia probably is of no value, and, even in the soil, the alkaloids which it represents may be actually injurious to growing plants.

By determining the water-insoluble theobromine plus caffeine it was found, as noted previously, that practically all of the alkaloid is readily extracted from the cocoa products by water at room temperature. The alkaloid nitrogen is therefore included with the water-soluble nitrogen. Wadsworth's results on the solubility of theobromine (*55*) also show that the pure base is sufficiently soluble in water for the total amount present in any of the samples to have been dissolved under the conditions governing the determination of water-soluble nitrogen, if the theobromine was present in the free or uncombined state. No attempt was made to determine whether the alkaloids were present in the free or combined state in the cocoa samples.

The amounts of total alkaloid found, ranged from 2.7 to 3.2 per cent for the press cakes (omitting the sample on which only theobromine was determined), 3.2 per cent for one extracted cocoa, and 1.6 and 2 per cent for the cocoa shells. Other work on cocoa products has indicated that the caffeine amounts to only about 5 per cent of the total alkaloid present.

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[27] In this connection it is of interest that a preliminary extraction with ether or petroleum ether rendered actually more nitrogen soluble in water for several of the samples.

PRACTICAL VALUE OF BY-PRODUCT COCOA CAKE

One of the two manufacturers of mixed fertilizer, known to have used the ground cocoa cake in commercial mixtures, reported that it gave satisfaction as a conditioner and crude ammoniate filler. This use of the press cake corresponds to the use of ground cacao shells in the fertilizer industry. The function of such material is to absorb moisture, produce a good mechanical condition in the mixed goods, and furnish organic ammonia in a form which becomes available gradually, thus insuring a more lasting supply of nitrogen. When asked if the large proportion of fat present in the material used had caused any trouble, this manufacturer stated that he had had no complaints, but that relatively small quantities of the cocoa were used in his mixtures.

The other user of cocoa cake as fertilizer material is one of the foremost concerns manufacturing complete fertilizers in the United States. This company, which uses ground cacao shells and dried solvent-extracted cocoa as "rough ammoniate" conditioners also, tried out the unextracted cocoa. The ground cake did not seem to be potentially as good a drying agent as the ground shells, but, of course, it supplied more organic nitrogen to the mixture. The selling price of the three cocoa by-products (ground shells, cake, and extracted cocoa) in the fertilizer trade is said to be based on the ammonia and potash content of the materials. The fertilizer concern mentioned was paying about the same price per unit of ammonia for cacao-shell meal and dried extracted cocoa as for "nitrogenous tankage," but considered the unextracted cake to be worth only about nine-tenths as much per unit of ammonia. A "unit" in the fertilizer trade is 1 per cent on a ton basis, or 20 pounds.

On this basis, under normal market conditions, the cocoa cake has a much higher value as fertilizer material than as fuel. As to the suitability of the cake for fuel, opinions of the manufacturers who have burned the product under their boilers differ markedly. There is ample testimony, however, to the effect that the relative fuel value of the cake, on paper, may be realized where the boiler-house engineer studies the character of the material as fuel and adapts his practices accordingly. At one large cocoa establishment there were loud protests from the engine room when use of the low-grade cake for fuel was discontinued because a more remunerative outlet for the product had been obtained.

Utilization of by-product cocoa as a fertilizer material is also in competition with its uses as a feed stuff and as a source of theobromine, therefore certain factors affecting its disposal through these channels are pertinent to this study. Feed mixers can afford to pay more than fertilizer manufacturers for the nitrogen in any organic material that they can use as a source of protein. Manufacturers of mixed feeds commonly endeavor to include in a mixture several dissimilar concentrates for furnishing protein, thus supplying variety in the feed. It was to have been expected, therefore, that cocoa cake, with its 4 per cent of nitrogen equivalent to 25 per cent of crude protein, would attract the attention of feed manufacturers as a possible new source of protein for their mixtures. In at least one case a consignment of the low-fat cake was purchased for use in a commercial mixed feed, of which it was to constitute 5 per cent, replacing higher-priced coconut cake as one of the protein-furnishing concentrates. The consignment of cocoa cake not only brought a higher price than would have been paid by the fertilizer trade, but in addition the cost of shipping it to the Pacific coast was paid. With the brokerage commission, this cocoa cake cost the feed manufacturer close to $30 per ton. Although cocoa is not being generally used in mixed feeds, the transaction cited illustrates the fact that when an organic ammoniate is wanted as a source of protein for mixed feeds, it commands a price well in excess of what the fertilizer manufacturer can afford to pay for it.

By-product cocoa, especially the dry-pressed or low-fat-content cake, containing around 3 per cent of theobromine, appears to be a very satisfactory raw material for the preparation of the alkaloid. For this purpose, however, the cocoa does not command as high a price as one might expect, considering the market quotation for the drug.[28] During 1924 the price paid for the dry-pressed cake by manufacturers of theobromine was reported to have been on a par with what the cake would have brought if sold for use as fertilizer material. Early in 1925, however, the writers were informed that the price asked for dry-pressed cake was getting above the maximum figure that the producers of theobromine could afford to pay. Irrespective of the selling price, however, the quantity of cocoa that can be consumed by drug manufacturers for the preparation of theobromine is limited by the demand for the alkaloid. Probably 1,000 to 2,000 tons of cocoa cake would yield all of the theobromine that the domestic market absorbs in a year. Incidentally it may be pointed out that the theobromine in ordinary cocoa cake, containing 18 per cent of fat, would be worth more than the cacao butter if both could be completely extracted and sold at current market prices.

The feasibility of extracting and recovering both the cacao fat and the alkaloids at one operation from by-product cocoa has been studied, and a method for accomplishing this was developed by a manufacturer of theobromine. The cacao fat recovered by this process was suitable only for soap stock, however, and as the method was not entirely satisfactory for the production of theobromine it was discarded and is not in use in the United States at the present time. The producers of theobromine do not now recover the cacao fat, and the concern engaged in extracting and preparing the fat from by-product cocoa cake is not extracting the alkaloids at the time of writing. An ideal system, economically, for the utilization of by-product cocoa cake would not only provide for the recovery of both the alkaloids and the fat in a pure condition, but would permit the retention in the extracted residue of the protein and other valuable constituents of the cocoa. Such a cocoa residue, from which the fat and alkaloids had been removed, but from which no other constituent had been lost, would have a higher value as fertilizer material, or for feeding purposes, than the original cocoa.

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[28] The quoted market price of theobromine alkaloid fluctuated between $3.60 and $4 per pound during the first quarter of 1925.

SOLVENT-EXTRACTED OR DEFATTED COCOA RESIDUE

NATURE, ORIGIN, AND PRODUCTION

The extracted or defatted cocoa residues that have been referred to consist of the cocoa matter that remains after extracting the fat from cocoa press cake or powder with a fat solvent. Cacao butter, because of its many desirable properties, vies with olive oil as the highest priced of the more common vegetable fats and oils produced in the United States. When, therefore, thousands of tons of cocoa cake, containing from 15 to more than 20 per cent of the valuable fat, became obtainable at a very low price, attempts to salvage the cacao fat on a commercial scale were bound to follow. Of the several fat-recovery processes tried out, however, only one based on solvent-extraction appears to have survived.

Only one concern is known to be operating commercially in the United States on the recovery of cacao fat from cocoa cake or powder. This company, which has been engaged with apparent success for more than a year in the enterprise, operates a plant with a capacity for extracting several thousand tons of cocoa annually. The process employed is sometimes referred to as the Scott or MacGregor system of extraction, and commercially pure benzol is used as the solvent. The equipment of the plant is very similar to and of the same type as that described by Chalmers (*10, p. 83–92*), and includes several large drum extractors, a solvent-recovery still with dephlegmator, tanks of special design for refining the fat, a sludge drier, grinding mills, and a refrigerating system.

The principal features of the process, in brief, are (1) the extraction of the powdered cocoa cake with benzol on the countercurrent principle, (2) separation of the solvent and dissolved fat from the extracted sludge by decantation, (3) recovery of the solvent by steam distillation, and (4) purification of the extracted cacao fat.[29]

After the solvent has been drawn off from the cocoa sludge as completely as possible, live steam is admitted to the extractor to volatilize and drive out the remainder of the benzol, so that it can be subsequently recovered by condensation. The crude, extracted cacao fat, after separation from the solvent, is subjected to very thorough refining. The refined product probably competes in the trade with ordinary cacao butter.

The steam treatment to which the material is subjected in the extractor cooks the moist defatted cocoa, converting it into a sludge, which, as it is discharged from the drum, contains about 65 per cent of water. This cooked, extracted cocoa is then dried in a direct-heat, rotary drum drier, if there is a market for it. Otherwise it is wheeled outside of the factory and piled in the open near the drier shed until there is a demand for the dried product. Figure 2 shows a large pile of the extracted-cocoa sludge that had accumulated during a period of slack demand. At the time of writing the only market for the dried sludge is that offered by the mixed-fertilizer industry. The material, like the related product, cacao shells, is used as a rough organic ammoniate conditioner and filler in complete fertilizer mixtures.

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[29] Certain novel features of the process are covered in United States Patents by Eddy (*13*), MacGregor (*32*), and Wilson (*59*).

Data on the quantities of cocoa cake extracted annually and the production of extracted sludge and dried extracted cocoa have been furnished by the producer, but these can not be published, as they relate to the operations of one concern only.

The yield of wet, extracted cocoa per ton of press cake extracted will vary somewhat with the amount of fat in the original cocoa cake, but from 1 ton of cake containing 18 per cent of fat about 2 tons of wet sludge containing 60 to 65 per cent of water would be produced. This would yield about 1,600 pounds of dried, extracted cocoa (with 8 per cent moisture), or 80 per cent of the weight of cocoa extracted.

Nothing whatever concerning solvent-extracted cocoa, its composition and properties, was found in the literature.

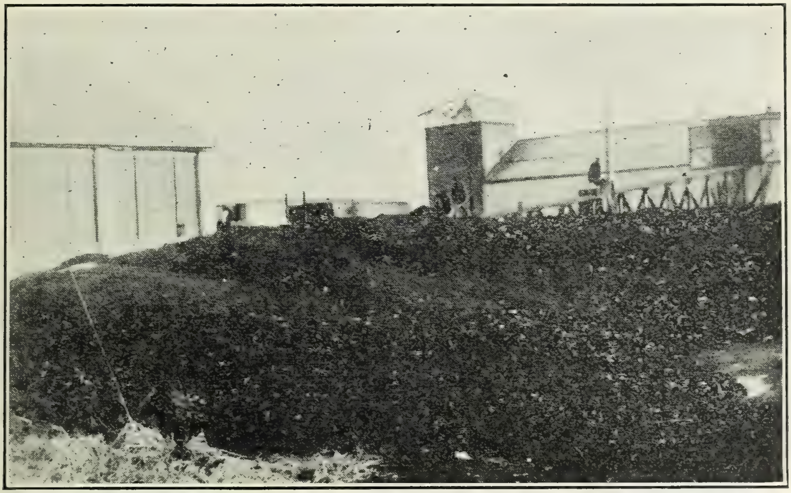

FIG. 2.—Accumulated extracted-cocoa sludge. This is the residue from solvent-extraction of the fat from by-product cocoa. The material is being wheeled to the drier shed, where it is prepared for the fertilizer market

Samples representing both the wet extracted cocoa and the dried material produced at the extraction plant have been examined and their nature is indicated by the analytical results given in Table 4. No attempt was made to have these samples represent the same batch of extracted cocoa, however. The data relating to the solubility and quality of the nitrogen of these samples are included in Table 3.

Sample 106 is the wet extracted sludge and its composition on both the wet and dry basis is shown. A portion of this sample was dried at 100° C. in the laboratory, and its composition corresponds to that of factory-made sludge dried without scorching or charring. Sample 107 was dried in the direct-heat rotary kiln at the factory and was decidedly charred. For this reason another sample (No. 116) of the commercial dried product which had been much less charred in drying was procured. Sample No. 101 is defatted cocoa that had been prepared in an industrial experimental plant.

TABLE 4.—*Composition and fuel value of solvent-extracted (defatted) cocoas*

Sample		Material as received									Fuel value data[1]	
No.	Description	Moisture	Ether extract (crude fat)	Petroleum ether extract	Nitrogen (total) expressed as ammonia, NH_3	Phosphoric acid (total) expressed as P_2O_5	Potash (total) expressed as K_2O	Ash	Crude fiber	Theobromine and caffeine alkaloids	Calorific value per kilogram	Volatile matter
		P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*Kgm.-cal.*	*P. ct.*
106	Wet, extracted cocoa sludge as produced at factory [3]	67.71	0.88	0.50	1.84	0.58	0.72	2.66	2.26	(4)	(4)	(4)
101	Dried material extracted in experimental plant	7.42	3.76	1.56	5.11	.98	1.99	6.29	(4)	(4)	4,382	65.82
106–A	Sample 106 dried in laboratory at 100° C	5.54	2.57	1.47	5.37	1.70	2.11	7.79	6.62	(4)	(4)	(4)
107	Commercial product extracted and dried at factory, partially charred [7]	6.46	3.35	2.17	5.34	2.11	2.52	11.65	(4)	(4)	4,760	[7] 54.1
116	Commercial product, less charred than sample 107	6.52	1.85	1.13	5.41	1.72	1.88	7.48	(4)	3.20	(4)	(4)
	Average, factory-extracted cocoa (3 samples)[8]	6.17	2.59	1.59	5.37	1.84	2.17	8.97	[9]6.62	[9]3.20	[9]4,382	[9]65.82

Sample		On dry, ether-extract-free basis						Ether-extract, volatile matter, and fuel value on dry, ash-free basis [1]			
No.	Description	Nitrogen (total) expressed as ammonia, NH_3	Phosphoric acid (total) expressed as P_2O_5	Potash (total) expressed as K_2O	Ash	Crude fiber	Theobromine and caffeine alkaloids	Ether extract (crude fat)	Volatile matter	Calorific value per kilogram	Calorific value of nonfatty organic matter for each per cent per kilogram [2]
		P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*Kgm.-cal.*	*Kgm.-cal.*
106	Wet, extracted cocoa sludge as produced at factory [3]	(5)	(5)	(5)	(5)	(5)	(5)	(6)	(6)	(6)	(6)
101	Dried material extracted in experimental plant	5.75	1.10	2.24	7.08	(4)	(4)	4.36	76.3	5,078	48.9
106–A	Sample 106 dried in laboratory at 100° C	5.84	1.85	2.30	8.48	7.2	(4)	(6)	(6)	(6)	(6)
107	Commercial product extracted and dried at factory, partially charred [7]	5.92	2.34	2.79	12.92	(4)	(4)	4.09	[7]66.1	5,813	[7] 56.6
116	Commercial product, less charred than sample 107	5.90	1.88	2.05	8.16	(4)	3.49	(6)	(6)	(6))	(6)
	Average, factory-extracted cocoa (3 samples)[8]	5.89	2.02	2.38	9.85	[9] 7.2	[9]3.49	[9]4.36	[9]76.3	[9]5,078	[9]48.9

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[1] The determinations of calorific value and volatile matter were made by H. M. Cooper, United States Bureau of Mines, on moisture-free samples. In this table his results have been correlated with the moisture and ash figures obtained on the original samples by the authors.

[2] The calorific value accepted for the ethyl-ether extract is 93 kgm.-cal. for each per cent per kilogram (9,300 Cal. per kilogram).

[3] This sample represents the wet cocoa residue after extraction of fat with benzol by the MacGregor process. The analysis was made on the material after drying in the laboratory at a temperature below 100° C. Only the results on the air-dry basis are included in the averages.

[4] Not determined.

[5] Same as for No. 106–A.

[6] Fuel value not determined.

[7] This factory-dried material also is a product of the MacGregor extraction process, but was partially charred in the drying. This accounts for the abnormally low volatile-matter content, and the high calorific value of the nonfatty organic matter, charcoal having a fuel value of about 7,000 Cal. per kilogram.

[8] The data for sample 101 were not included in the averages.

[9] For one sample.

DRYING THE EXTRACTED SLUDGE

The favorable effect on the composition of the dried product of drying the sludge at the lower temperatures that prevail in steam-heated driers is obvious, but the nature of the extracted cocoa presents a serious obstacle to drying large batches of the material by steam heat. As a first consideration, the cost of drying must be kept low, because of the comparatively low value of the dried product, and this is said to preclude the employment of a vacuum drier. But steam heat without the aid of a partial vacuum in the drier is reported to be ineffectual, as the physical condition of the sludge is such that, while a lump of it will dry readily on the immediate surface, the crust thus formed protects the doughy interior from further dehydration. On the other hand, the higher temperatures prevailing in the direct-heat rotary drier make it both effectual and economical, but its use is attended by some charring of the product.

Certain effects of charring on the properties of the dried cocoa sludge are shown in Tables 3 and 4. Charring accounts for the abnormally low content of volatile matter of sample 107, which means a higher percentage of fixed carbon, as the latter is merely the total organic matter less the volatile matter. This in turn accounts for the high calorific value found for the nonfatty organic matter of this sample, the fixed carbon of such material being practically the same as charcoal, which has a calorific value of about 7,000 Calories per kilogram. That charring also slightly depresses the solubility in water of the nitrogen is indicated by a comparison of the results reported for the several extracted cocoas in Table 3 (although more significance could be attached to these results if the samples were from the same lot of extracted cocoa). On the other hand, the solubility of the nitrogen in sample No. 106 was somewhat increased by drying at 100° C. This apparent increase in solubility may be due to the fineness of the particles after drying and grinding.

UTILIZATION OF EXTRACTED COCOA

Laboratory tests with unextracted cocoas showed that, for a particular sample, the solubility in water of the nitrogen was increased somewhat by a preliminary extraction of the fat with ether or petroleum ether. This is merely additional evidence in support of the theory that fat or oil, when present in large quantity in a fertilizer material of this type, tends to envelop and waterproof the particles containing plant food, delaying their dissolution when the material is applied to the soil and thus lowering the availability of the fertilizer constituents. It is to be noted that the true fat content of the commercial, dried, extracted cocoa averages less than 2 per cent.

The factory-dried extracted cocoa contains about 5.4 per cent of total "ammonia," as against 4.8 per cent for the average ammonia content found for all of the by-product cocoa cake samples examined. Two of the samples of dry-pressed cake, however, contained as much ammonia as the defatted residues; and on the basis of the dry, fat-free matter the straight cocoa press cakes surpass the extracted product in ammonia content.

Most, if not all, of the potash is retained and recovered in the extracted residue. This is accounted for by the fact that the water with which the cocoa becomes mixed during the extraction operation is absorbed by the cocoa matter and the dissolved salts remain with the sludge when the latter is dried. In view of this retention of plant-food elements, and the elimination of most of the fat, the dried solvent-extracted cocoa undoubtedly has a higher value as fertilizer than unextracted cocoa.

The retention of the theobromine and caffeine in the sludge is explainable on much the same grounds as the retention of the mineral salts. Theobromine is far more soluble in water than in benzol, according to Wadsworth (*55*), and it appears that little if any alkaloid is lost from the cocoa matter in the solvent-extraction of the fat. Although the retention of the alkaloids in the extracted cocoa creates a certain value for the product as raw material for the preparation of theobromine, the presence of the alkaloids is an obstacle to utilization of the product as a feed stuff and detracts from its intrinsic value as a source of plant food.

The permanency of the commercial production of solvent-extracted cocoa depends, of course, on the ability of the extraction industry to continue to solve the major problems as they appear. One of the problems that is receiving attention is that of finding more profitable outlets for marketing the defatted cocoa by-product. As pointed out above, the dried extracted cocoa obviously has a higher value for use as fertilizer material than the unextracted cocoa cake, as it contains more total ammonia, potash, and phosphoric acid, and is nearly free from the undesirable fat. Comparison of the data on the solubility and quality of the nitrogen of the sample dried at 100°C. and the kiln-dried sample (Nos. 106–A and 107, Table 3) indicates, however that the quality of the factory product could be somewhat enhanced by drying at lower temperatures to avoid charring. It appears, therefore, that one opportunity for improving the marketability of the extracted cocoa by-product lies in devising means for dehydrating the sludge at lower temperatures, but at a cost commensurate with the commercial value of the product.

The theobromine and caffeine content of the dried extracted cocoa is shown by the data in Tables 2 and 4 to be about on par with that of the by-product cocoa cake. This fact, together with the low fat content of the solvent-extracted material, suggests that it is very well suited for use as raw material for the preparation of theobromine alkaloid. With the process now in use for the commercial production of theobromine, the presence of fat in the raw material is undesirable.

The materials used at present as a source of theobromine, with which the extracted cocoa would have to compete in this field, are the by-product press cake and cacao shells. Dry-pressed cocoa cake is preferred to the commercial shells, in spite of its somewhat higher fat content, because it usually contains from 50 to 100 per cent more of the alkaloid than the shells.[30] Obviously, the dried, extracted-cocoa residue would occupy a very advantageous position in competition with either of these products; for, on the basis of the samples examined, it compares well with the dry-pressed cake and is superior to cacao shells in alkaloid content, and its content of the objectionable fat is almost negligible.

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[30] Wadsworth (*57*) reports the average theobromine content of 31 samples of separated cacao shells as 1.27 per cent, and that of commercial cocoa powders (23 samples) as 2.10 per cent. Many investigators have reported the theobromine content of cacao shells to be under 1 per cent.

It is reasonable to suppose that dissemination of this information may be followed by the advent of a new market outlet for the solvent-extracted cocoa residue, through its use as raw material in the commercial production of theobromine alkaloid. It may therefore be of interest to point out that the cocoa matter remaining from such utilization, having been freed from both fat and alkaloids, will have attained maximum value as fertilizer material, provided no important loss of plant-food constituents has taken place during the extraction of the alkaloids. Investigation of this contingency, however, necessarily must wait upon use of the solvent-extracted cocoa by the producers of theobromine, because of lack of knowledge of the treatment to which the material would be subjected in the commercial preparation of the alkaloid.

CACAO (OR COCOA) SHELLS

NATURE OF THE BY-PRODUCT

Raw cacao beans, as imported into the United States, contain from 7 to 16 per cent by weight of shell. This refers to clean, unclayed beans. The shell content of average unclayed beans may be taken as 12 per cent, and a large part of the cacao imported will not show great variation from this figure. Besides the shell material, average cacao beans contain about 0.7 per cent by weight of the hard radicle or germ.

Roasting the beans decreases the weight of shell somewhat, and it may be assumed that for every 100 pounds of raw cacao used, there are between 10.5 and 11 pounds of roasted shells in the beans when they go to the cracking and separating machines.

After roasting, the shells and nibs are brittle, and it follows that a certain amount of fine material (composed of both shell and nib) results from the breaking and handling by machinery of the roasted beans. Such fine material is known as "dust" or "fines" in this country and is usually handled independently of the shells.[31] Combined with the separated germs, the product is known in England as "smalls."

The relative amounts of shell material, usable nibs, and fines produced vary with the kind of beans and the equipment and milling practice in the factory. As stated in the general discussion of the manipulation of the beans, perfect separation of shells and nibs is never attained in factory practice. Under the best conditions, the separated nibs may contain as much as 2 per cent of practically inseparable shell material, and the shell portion will contain an appreciable quantity of nib material.

Reports have been received from cocoa and chocolate manufacturers showing that the quantity of the separated shells portion produced varies from 6 to 12 per cent of the weight of raw beans. The quantity of fines obtained to a certain extent is supplemental to the quantity of separated shells. Where the shells amounted to 6 or 7 pounds per 100 pounds of raw cacao, the fines amounted to 6 or 7 pounds, but where 12 pounds of commercial shells were obtained the fines amounted to little more than the weight of the germs. Probably Knapp's data are about as true for average American practice as they are for conditions in English factories. He reports (*24*) the production of 10.5 pounds of separated shells and 4 pounds of smalls or fines per 100 pounds of raw cacao.

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[31] This minor by-product in the preparation of the nibs is sometimes pressed for its contained fat in this country. United States Patent No. 1467587 covers a novel process for pressing this type of cocoa material (*1*).

QUANTITY OF COMMERCIAL SHELLS PRODUCED

The imports of crude cacao into the United States for the calendar years 1923 and 1924 were 207,118 and 189,141 short tons respectively, or, in round numbers, about 200,000 tons[32] of the beans per year (*54, p. 48*).

Since from 6 to 12 pounds of shells are produced per 100 pounds of raw cacao, it follows that the production of factory-separated shells in the United States amounts to between 12,000 and 24,000 tons annually. Estimating the quantity of commercial shells at 10 per cent of the weight of raw beans, it may be assumed that since the World War from 15,000 to 20,000 tons of cocoa shells have been produced each year in this country.

UTILIZATION

Cocoa shells, unlike the by-product cake and extracted cocoa, have long been recognized as an established article of commerce. Large quantities of the ground shells, known as cocoa-shell meal, are consumed in the manufacture of commercial mixed fertilizers. A certain quantity is used in this country in the preparation of proprietary feed mixtures, particularly in goods of the calf-meal type. Cacao shells also have been used by manufacturers of theobromine for the extraction of the contained alkaloid, but are considered less valuable for this purpose than the low-fat pressed cake. (See p. 27.) Most of the shells produced in the United States, it is believed, are consumed in the three ways mentioned.[33]

Doubtless the shells are occasionally burned for fuel under the boilers in the producing factories. The value of the shells for this purpose, like that of the cocoa cake, would be influenced by their fat content. Knapp has stated that cacao shells have a slightly higher value than wood as fuel, the heat of combustion being 7,400 to 8,600 B. t. u. per pound for the shells (*24*).

COMPOSITION AND AGRICULTURAL VALUE OF SHELLS

There is little specific information relating to the value of cacao shells as fertilizer material to be found in the literature. The

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[32] The relative magnitude of this tonnage is shown by comparing it with the annual production of regular American crops. In 1923 the imports of cacao were equal in weight to 44 per cent of the total dry or navy bean crop or to 64 per cent of the peanut production of the country.

[33] One manufacturer of chocolate mentioned an odd experience in connection with disposal of the shells, which, while seemingly trivial in relation to quantity utilization, may be of some significance. Some of the shells were used as bedding for dogs. Later the keeper credited the cocoa shells with having caused the disappearance of fleas with which the animals had been infested. This suggests the possibility that the shells may contain a chemical principle repellant to certain insects.

Canada Experimental Farms report for 1898 contains an analysis showing the crude fertilizer and feed constituents of a sample of the by-product (*42*); and a similar analysis is given by Lindsey and Smith of the Massachusetts Agricultural Experiment Station (*28*). Cathcart, of the New Jersey station, investigated the solubility and quality of the nitrogen in a factory sample reported as cocoa shells (*8, p. 45*).

The Canadian analysis showing a content of 12.9 per cent of fat and 2.63 per cent of nitrogen indicates that the material contained an appreciable quantity of the nibs and was comparable with much of the commercial cocoa-shell meal now being used in fertilizers. This sample contained 1 per cent of phosphoric acid (P_2O_5) and 2.6 per cent of potash (K_2O). The analysis given by Lindsey and Smith, which is the average for two samples, shows their material to have been of the same type. The average figures were—nitrogen, 2.45 per cent, of which about one-third was rated available; phosphoric acid. 0.7 per cent; and potash 2.9 per cent. The New Jersey sample, on the other hand, contained only 1.92 per cent of nitrogen and undoubtedly represents a lower-grade product, as even pure cacao shell usually contains more nitrogen than this, and the presence of nib or germ would increase the nitrogen content. Phosphoric acid was found to the extent of 0.6 per cent. The quality of the nitrogen was investigated by the alkaline permanganate method, with the following results: Water-soluble nitrogen, 0.35 per cent; active insoluble nitrogen, 0.34 per cent; inactive insoluble nitrogen, by difference, 1.23 per cent (*8, p. 45*). This checks the Massachusetts figure for the "availability" of the nitrogen, as the sum of the water-soluble and active nitrogen amounts to about 36 per cent of the total nitrogen.

An actual field test of the value of cacao shells as a soil amendment is mentioned in a number of books on cocoa and chocolate. The experiment, which was made at Bournville, where one of the great English chocolate factories is located, showed, according to Knapp (*26*), that the availability of the plant food contained in cacao shells can be improved by keeping the shells in heaps soaked with water and turning over the mass from time to time. Shells that were applied directly to the soil, without previous soaking, did not decompose readily and yielded their plant food very slowly, whereas the shells that had been subjected to wet composting were in a decomposed condition when applied and gave good results, particularly when used to lighten heavy soil.

Much more space in the literature of cocoa and chocolate has been devoted to discussion of the use of cacao shells in the feeding of animals than as fertilizer material. A reason for this is found in the fact that a great deal of the published work is of English and continental European origin; and Knapp has stated that the bulk of the cacao shells produced in England is used in the manufacture of mixed stock feeds (*26*, *27*). Below are given brief summaries of the more important references found in the literature relating to the feeding of cacao shells.

Albert (*2*) reported in a German periodical, in 1899, that the shells were a satisfactory auxiliary feedstuff for steers. Dean (*11*), of the Ontario Agricultural College, as a result of feeding experiments in 1903, suggested the employment of cocoa shells in the preparation of a substitute for skim milk for calves. Lucas (*29*) replaced 3.3 pounds of wheat bran, in the ration of dairy cows, with 4.4 pounds of cacao shells, with the result that the flow of milk was materially decreased. He concluded that the unfavorable effect of the shells was due not only to their low nutritive value, but to the presence of a substance inimical to milk secretion.

Data on the amounts of digestible nutrients in cacao shells were reported by Kellner many years ago. More recently, Lindsey and Smith, of the Massachusetts station, working with sheep, determined the actual percentage of digestibility (coefficients of digestibility) of the nutrient constituents of commercial cocoa shells (*28*). They also fed shells to dairy animals and found that from 1 to 3 pounds, mixed with grain, could be fed daily.

The alkaloid content of the shells, in relation to their use as stock food, seems to have been ignored in these earlier investigations cited, and scant consideration appears to have been given to the possible toxic action of the theobromine and caffeine until, during the World War, several French army horses were fatally poisoned, following the feeding of 1.5 kilograms (3.3 pounds) of shells per day. Marchadier and Goujon (*33*), who were the first to report the poisonings, made a study of the toxicity of the shells in connection with one of the cases, in which seven horses died. The shells under suspicion were found to contain (average) 0.68 per cent of theobromine and 0.22 per cent of caffeine; so that each horse ingested 13.5 grams of the alkaloids per day, or a total of 54 grams in the four days preceding death. The investigators concluded that the deaths were caused by the alkaloids in these cacao shells, and they suggest that the absence of ill effects following the feeding of shells to horses by earlier investigators may have been due to a lower alkaloid content of the shells used (Compare Zipperer (*61*)). Another case of poisoning of French army horses is reported by Fonzes-Diacon, who found 0.7 per cent of theobromine in a sample of the cacao shells that had been fed to the horses (*15*).

Later, Rothéa (*40*) reviewed both of the preceding investigations, and reported the analysis of a sample of ground cacao shells which he found to contain 1.09 per cent of theobromine. This material contained 9.36 per cent of fat, and 2.77 per cent of nitrogen, and may therefore have contained an appreciable amount of cacao nib, and have been comparable to some of the " cocoa-shell meal " marketed in America. Rothéa also suggests that the residues of shells made safe for feeding through extraction of the alkaloids would have but slight nutritive value.

One of the latest reports on the suitability of cocoa by-products for feeding purposes is that by Griffiths (*17*). After summarizing much of the preceding work, he concludes that the use of cocoa shells and meal as a feed stuff " can not be considered." A number of proximate feed analyses of cocoa shells are to be found scattered through recent experiment station reports (*9, p. 10; 35, p. 230; 43, p. 69*). For the most part these show that commercial shells generally contain appreciable quantities of nibs.

RESULTS OF THE PRESENT INVESTIGATION

Two samples of cocoa shells believed to be representative of the commercial product were obtained. One was furnished by a manufacturer of cocoa and chocolate, and represented the average run of his shells by-product. The other was a sample of a lot of cocoa-shell meal that had been purchased in the usual course of business by a manufacturer of commercial fertilizers.

These samples were analyzed not only to furnish information as to the type of product being marketed as cocoa shells in this country, but also to obtain data that would provide a standard with which to compare (for commercial purposes) the analyses of the relatively unknown cocoa press cake and extracted cocoa. It was thought that the shells, being a product closely related to the press cake and extracted cocoa, would serve admirably as a control material, by which to gauge the relative fertilizer value of the last-named products.

The results of a proximate analysis of the two samples of shells are given in Table 5; and the data on the solubility and quality of their nitrogen are included in Table 3.

TABLE 5.—*Composition of commercial cacao shells*

Sample		Material as received								
Number	Description	Moisture	Ether extract (crude fat)	Petroleum ether extract	Nitrogen (total) expressed as ammonia, NH_3	Phosphoric acid (total) expressed as P_2O_5	Potash (total) expressed as K_2O	Ash	Crude fiber	Theobromine and caffeine alkaloids
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
115	Shells from roasted Bahia beans, from factory	2.87	9.15	8.55	3.61	1.23	2.52	8.30	15.64	2.0
117	Commercial cocoa-shell meal	5.25	9.29	8.53	3.33	1.26	2.21	8.12	16.23	1.6
	Average (2 samples)	4.06	9.22	8.54	3.47	1.25	2.37	8.21	15.94	1.8

Sample		On dry, ether-extract-free basis					
Number	Description	Nitrogen (total) expressed as ammonia, NH_3	Phosphoric acid (total) expressed as P_2O_5	Potash (total) expressed as K_2O	Ash	Crude fiber	Theobromine and caffeine alkaloids
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
115	Shells from roasted Bahia beans, from factory	4.1	1.40	2.86	9.43	17.78	2.27
117	Commercial cocoa-shell meal	3.9	1.47	2.59	9.50	18.99	1.87
	Average (2 samples)	4.0	1.44	2.73	9.47	18.39	2.07

The amounts of fat, crude fiber, and total "ammonia" found in the samples indicate the presence of important quantities of nib material. The proportion of nibs in a sample of this kind can best be estimated from its fat content, since the spread between the fat content of pure shells and pure nibs is much greater than the spread for any other constituent whose percentage in the samples was determined. Assuming 53 per cent as the fat content of pure roasted nibs, and accepting 3.5 per cent (the average reported figure) as the fat content of pure shells, it follows that the two samples of commercial shells (Nos. 115 and 117) with a fat content of about 8.5 per cent, must contain approximately 10 per cent of nibs. The presence of this quantity of nib material in these samples of commercial cocoa shells accounts for the favorable analytical results obtained in the laboratory determinations of the solubility and quality of their nitrogen. It may be noted, for example, that relatively much more soluble and active insoluble nitrogen was found in these samples than Cathcart (*8*, *p. 45*) found in the sample discussed on page 35, which must have contained little or no nib material.

Comparison of the composition of the shells samples (Table 5) with the average composition of the cocoa press cakes, as given in Table 2, shows that these commercial cocoa shells contained less than three-fourths as much total "ammonia," slightly less phosphoric acid, but appreciably more potash than the average for by-product press cake. The shells also contain more potash than the dried extracted cocoas (Table 4), but only about two-thirds as much ammonia and phosphoric acid.

The percentage solubility of the nitrogen of these commercial shell samples, it will be noted from Table 3, is a little less and the quality of the insoluble nitrogen is somewhat lower than is the case with the by-product press cakes and solvent-extracted cocoas; but the differences are hardly sufficient to affect adversely the relative market value of a unit of ammonia in shells in comparison with that of a unit of ammonia in the other cocoa materials.

A unit of ammonia in the commercial shells or cocoa-shell meal, as a matter of fact, commands a slightly higher price in the fertilizer materials market than a unit of ammonia in the cocoa press cake; whereas the ammonia in the commercial extracted cocoa ordinarily has been rated at the same price per unit as that in the shells. The reason that cocoa shells, in spite of the slightly lower quality of their nitrogen, can maintain a better price per unit than the by-product cake, is to be found in the better physical condition of the shell material after grinding. Shell meal is a good absorbent material and drier and, being more fibrous than cocoa powder, it has less tendency to get sticky in moist mixtures. It is porous and very light in weight, 1 cubic foot of the powdered shells weighing only 32 pounds, according to Knapp (*24*). These properties and the fact that the material has a dark, rich color recommend the shells to commercial fertilizer mixers. As a conditioner for mixed fertilizers and "rough ammoniate" filler, cocoa shells appear to have given satisfaction to fertilizer manufacturers using them.

An estimate has been made of the relative market value for fertilizer purposes of shells, press cake, and extracted cocoa, based on the current prices for ammonia and potash in this type of material. Assuming the price for a unit of ammonia in press cake to be 90 per cent of that for a unit in shells or in extracted cocoa, and using the average figures for the ammonia and potash contents of the three materials (Tables 2, 4, and 5), the relative market values are found to be as follows: (1) By-product cocoa press cake of average composition would bring 20 per cent more per ton than commercial cocoa shells like the samples; and (2) dried solvent-extracted cocoa would bring 50 per cent more per ton than these shells. For use as fertilizer material, average press cake, therefore, might be expected to bring 80 per cent of the price of the solvent-extracted cocoa per ton.

Shells with a lower ammonia content would, of course, have a relatively lower market value than those represented by the samples examined, on which the foregoing estimates were based, since the market price is mainly dependent on the content of ammonia.

SUMMARY

Until a few years ago the only cacao by-product in the United States having a sufficiently low market value to be available to the fertilizer manufacturer was the shells, with such related waste material as cocoa dust and sweepings. As a result of the enormous demand for cacao butter, two additional by-products of importance are now being produced in large quantities and are available at prices which make them of interest as fertilizer materials. These are the by-product cocoa press cake and solvent-extracted cocoa. The latter is the defatted residue left after extracting the cacao fat from the press cake with benzol.

It is estimated that the annual production of by-product cocoa cake was between 15,000 and 21,000 tons in 1923, and 25,000 tons in 1924. Two main types of press cake are being produced: The more common, higher fat content sort; and the dry-pressed cake, which is turned out by very powerful presses and has a much lower percentage of fat. A certain quantity of cocoa dust and fine waste, also, is pressed for its fat, resulting in a lower grade of press cake.

A single cursory factory test indicated that under certain conditions a better yield of fat could be obtained by grinding and pressing whole cacao beans.

Quantities of the cake of the higher fat content types are utilized for recovery of the fat by solvent extraction, and a part of the low-fat type has been in demand for use as raw material for the preparation of the alkaloid theobromine.

Including the cake subjected to solvent extraction, the residue from which is utilized as fertilizer material, it is estimated that at least one-fourth of the by-product cake produced is eventually consumed in fertilizer. A smaller quantity was used in mixed feeds during 1924; and some was used in the preparation of theobromine. Some by-product cake has been burned as fuel by the manufacturers.

Utilization of cocoa by-products as fertilizer materials, therefore, is in more or less active competition with their use as feed stuffs, as sources of the alkaloid theobromine, and to a lessening extent as fuel.

The few tests that have been reported in the literature on the feeding value of cocoa cake show that it depresses the milk flow of dairy cattle. A review of the literature leads to the conclusion that caution should be observed in feeding cocoa products to animals, especially to nonruminants.

The present investigation included chemical examination of representative cocoa press cakes, solvent-extracted cocoas, and cacao shells. Several of the samples of press cake satisfied the chemical requirements for edible cocoa powder. The average calorific value of the press cakes was found to be about two-thirds that of good bituminous coal; and it has been found feasible to calculate the calorific value of the cocoas from their moisture, fat, and ash contents, through the employment of a constant determined in this investigation.

More than one-third of the total nitrogen of both the pressed cake and solvent-extracted cocoa was found to be water-soluble, but the insoluble organic nitrogen, on the basis of its "activity" measured by either of the permanganate methods, was found to be of inferior quality. Also it is shown that the alkaloid nitrogen is included in the water-soluble nitrogen, of which it may constitute 50 to 60 per cent. The sum of the water-soluble and active insoluble nitrogen made up a somewhat smaller share of the total nitrogen in the cocoa press cakes and extracted cocoas, than in the cases of samples of cottonseed meal and castor pomace for which such data have been reported in the literature reviewed.

The cocoa press cakes were found to contain, as the average, about three-fourths as much nitrogen and phosphoric acid, and twice as much potash as castor pomace; and to be similar to commercial "cottonseed feed" in crude plant-food content.

Theobromine and caffeine were found to be present in cocoa by-products in quantities significant in relation to use of the materials either as feeding stuff or as fertilizer material. Laboratory work demonstrated that practically all of the alkaloid in the samples examined readily dissolved in water at room temperature.

Ground cocoa cake is reported to have been satisfactory when used as a "rough ammoniate" filler and conditioner in mixed fertilizers; and the material had a decidedly higher monetary value as fertilizer material than as fuel. Where the cake has been marketed for use as an ingredient of mixed feed, it has brought a higher price than it commanded as fertilizer material or as raw material for the preparation of the alkaloid theobromine.

It is suggested that an ideal system for the utilization of by-product cocoa cake would provide for—(1), recovery of the fat; (2), recovery of the alkaloids; and (3), retention of the valuable food and fertilizer constituents in the defatted, dealkaloidized residue.

One concern is engaged, commercially, in recovering cacao fat from cocoa press cake by solvent extraction; and an important quantity of the dried, extracted residue is being produced. Part of the output of extracted cocoa has been used as a crude ammoniate filler and conditioner in mixed fertilizers, and for this purpose the material seems to have been satisfactory to the mixers.

Representative samples of the factory-made product examined show that very nearly the entire content of each of the plant-food constituents and of the alkaloids present in the original cocoa cake is retained in the defatted by-product. Hence this by-product, being nearly fat-free, contains more plant food and has a higher value as fertilizer material than average unextracted cocoa. The presence of the alkaloidal bases in the solvent-extracted cocoa suggests that it may have value as raw material in the preparation of theobromine, but detracts from its intrinsic value as a source of plant food.

The solubility or quality of the nitrogen of the solvent-extracted residue is a little lower than that of the cocoa cake.

Cacao shells, as separated in the factory, amount to about 10 per cent of the weight of raw cacao beans, so that some 20,000 tons of commercial shells are produced annually in the United States. Large quantities of the ground shells, known as cocoa-shell meal, are utilized as conditioning material in the manufacture of commercial fertilizers. The shells have been used as a feed stuff, but are of low nutritive value; and several French army horses are reported to have been fatally poisoned by the alkaloids present in shells fed them.

Two samples of shells, believed to be representative of the commercial product, on analysis, were found to contain about 10 per cent of nib material.

The shells contained less than three-fourths as much nitrogen, a little less phosphoric acid, and appreciably more potash than the average by-product cocoa cake. The quality of the nitrogen of the shells was lower than that of the cake and extracted-cocoa nitrogen.

The relative market value for fertilizer purposes of average commercial by-product cocoa cake, dried extracted cocoa, and shells is estimated to be as 1.2 to 1.5 to 1.0—on the basis of current prices for ammonia and potash in this type of material.

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